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INDIAN AGRICULTURAL
RESEARCH INSTITUTE, NEW DELHI

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THE
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OF
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FROM JANUARY 1938 TO NOVEMBER 1938

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CAPT. C. W. HUME, M.C., B.Sc.

Assistant Secretary:

MISS J. I. DENNIS

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PROCEEDINGS AT THE MEETINGS OF THE PHYSICAL SOCIETY

SESSION 1937-38

*Except where the contrary is stated the meetings were held at the Imperial
College of Science and Technology, South Kensington,
the President being in the Chair.*

8 October 1937

H. G. Kuhn was elected to Fellowship of the Society.

The President announced that Council had elected the following to Student Membership of the Society: R. E. Burgess, Dennis Albert Nicholls, Frederick Haydn Vanstone.

The following papers were read:

"The electric charges on single raindrops and snowflakes", by J. A. CHALMERS, M.A., Ph.D. and F. PASQUILL, B.Sc.

"The kinetic theory of fluids", by S. C. BRADFORD, D.Sc.

The following papers were read in title:

"The measurement of the intensities of x-ray reflections from crystalline powders in absolute units", by G. W. BRINDLEY, M.Sc., Ph.D. and F. W. SPIERS, Ph.D.

"The electrical resistance of manganese amalgams", by L. F. BATES, D.Sc., Ph.D., F.Inst.P. and P. G. DAY, B.Sc.

"The magnetic properties of silver amalgams", by L. F. BATES, D.Sc., Ph.D., F.Inst. P. and A. W. IRELAND, B.Sc.

Prof. H. FREUNDLICH gave a demonstration entitled "Wettability in flotation".

22 October 1937

The President announced that Council had elected the following to Student Membership of the Society: Edwin Allard, P. Howard-Flanders.

The Twenty-second Guthrie Lecture was delivered by Dr C. C. PATERSON, O.B.E., M.I.E.E., F.Inst.P., of the Research Laboratories of the General Electric Company Limited, who took as his subject "The Appraisalment of lighting".

12 November 1937

The following were elected to Fellowship of the Society: Alexander Keir Longair, George Thomson Purves, Raoul Frederic Schmid, William John Thomas.

It was announced that Council had elected R. C. Pankhurst to Student Membership of the Society.

Proceedings at meetings

The following papers were read:

"The surface structure of liquid mercury", by G. L. J. BAILEY, S. FORDHAM and J. T. TYSON.

"The ratio of the masses of the fundamental particles", by H. T. FLINT, D.Sc.

The following papers were read in title:

"Atomic scattering factors of aluminium, potassium chloride and copper for x rays", by G. W. BRINDLEY, M.Sc., Ph.D. and P. RIDLEY, B.Sc.

"A note on the optimum counting-time for measuring the intensity of a radioactive source", by J. TANDBERG.

A demonstration of structures proposed for protein molecules was given by Dr DOROTHY M. WRINCH.

26 November 1937

Meeting held in the Physics Department, London (R.F.H.) School of Medicine for Women, 8 Hunter Street, London, W.C.1 (by kind invitation of the Council and Miss M. D. Waller).

The following were elected to Fellowship of the Society: Neville Samuel Billington, Edward Roy Davies, Rhisiart Morgan Davies, Patrick Docksey, Arthur Robert Hogg, Oliver Owen Pulley, James Harvey Nelson (transfer from Student), John Richard Tillman (transfer from Student).

The following paper was read:

"Vibrations of free circular plates", by Miss M. D. WALLER. Part I. Normal modes. Part II. Compounded normal modes. Part III. A study of Chladni's original figures.

The following papers were read in title:

"The nature of fatigue in the auditory system", by R. C. PARKER, Ph.D.

"An impedance magnetometer", by E. P. HARRISON, Ph.D., F.Inst.P. and H. ROWE, B.Sc.

"On the dependence of the rate of viscous flow of metals on the deforming force, and its variation with temperature. Part I. Tin", by L. C. TYTE, B.Sc., Ph.D., F.Inst.P.

"Note on the theory of photo-conductivity", by N. F. MOTT, F.R.S.

The following demonstrations were given:

(i) Magneto-damping in nickel, by Miss M. D. WALLER.

(ii) A demountable plane-electrode thermionic tube used as a generator of ultra-high-frequency oscillations, by Dr W. A. LEYSHON.

9 December 1937

Meeting held in the theatre of the Royal Institution, 21 Albemarle Street, London, W.1, by kind permission of the Managers.

The Thomas Young Oration was delivered by R. J. LYTHGOE, M.A., D.Sc., M.D., B.Ch., of University College, London, who took as his subject "The structure of the retina and the role of its visual purple".

4, 5, 6 January 1938

The Twenty-eighth Annual Exhibition of Scientific Instruments and Apparatus was held at the Imperial College of Science and Technology.

The following discourses were delivered:

"The mechanical amplification of small displacements", by Professor A. F. C. POLLARD.

"Diving in deep water and shallow", by Captain G. C. C. DAMANT.

28 January 1938

Werner Arthur Schneider was elected to Fellowship of the Society.

The prizes and certificates awarded for the ninth Competition in Craftsmanship and Draughtsmanship were presented.

A demonstration of a laboratory method for the determination of the period of transverse oscillations of flexible rods by means of a photoelectric cell was given by J. E. CALTHROP, M.A., M.Sc. and G. A. BENNETT, B.Sc.

The following papers were read:

"The whispering gallery of St Paul's Cathedral, London", by A. E. BATE, Ph.D., M.Sc., F.Inst.P.

"The variation of voltage-distribution and of electron transit time in the space-charge-limited planar diode", by R. COCKBURN, M.Sc., A.Inst.P.

The following papers were read in title:

"The sparking potential of mercury vapour", by F. LLEWELLYN JONES, M.A., D.Phil. and W. R. GALLOWAY, B.Sc.

"The diurnal variation of the ionospheric absorption of wireless waves", by J. E. BEST, Ph.D. and J. A. RATCLIFFE, M.A.

"High-latitude radio observations", by A. B. WHATMAN, B.A. and R. A. HAMILTON, B.A.

"The evaluation of some hexagonal structure factors", by C. A. BEEVERS and H. LIPSON.

"The application of the absorption method to the determination of the upper limits of continuous β -ray spectra", by E. E. WIDDOWSON, M.Sc. and F. C. CHAMPION.

11 February 1938

The following were elected to Fellowship of the Society: Albert Leslie Beedle, Samuel Clement Bradford, John Britton Carne, Arthur William Carter, Constance Griffiths, Victor F. Hess, E. J. A. Kenny, Leslie Thomas Minchin, Robert

Rutherford Nimmo, James Huntley Phillips, David Arthur Bell (transfer from Student), Alfred Gordon Gaydon (transfer from Student).

The President announced that Council had elected Edwin John le Fevre to Student Membership of the Society.

A demonstration was given by R. W. B. PEARSE, Ph.D. and A. G. GAYDON, Ph.D. of two types of discharge tube of high intensity for the production of molecular spectra (i) for use with gases, (ii) for use with refractory substances.

The following papers were read:

"Prevention of sound-transmission along water pipes", by J. E. R. CONSTABLE, M.A., B.Sc., Ph.D.

"Transmission of sound in a building by indirect paths", by J. E. R. CONSTABLE, M.A., B.Sc., Ph.D.

"The electrical reproduction of images by the photoconductive effect", by H. MILLER, M.A., Ph.D. and J. W. STRANGE, B.Sc., A.R.C.S.

The following papers were read in title:

"The spectrum of manganese hydride, MnH ", by R. W. B. PEARSE, Ph.D. and A. G. GAYDON, Ph.D.

"Sensitivity of photographic plates in the region 2500 to 2000 \AA .", by A. HUNTER, Ph.D. and R. W. B. PEARSE, Ph.D.

"On the equilibrium of a ball supported by a vertical air jet", by G. D. YARNOLD, M.A., D.Phil.

"Rotational analysis of the bands of lead sulphide", by H. BELL, M.A. and A. HARVEY, Ph.D., F.Inst.P.

25 February 1938

The following were elected to Fellowship of the Society: H. P. Barasch, H. L. Penman, R. A. Buckingham (transfer from Student).

The President announced that Council had elected I. Sharpe and J. C. Weston to Student Membership of the Society.

The Presidential Address was delivered by THOMAS SMITH, M.A., F.Inst.P., F.R.S., who took as his subject "Vision through optical instruments (including the unaided eye, spectacles and more complex systems)".

The following papers were read in title:

"Dissociation energy of the CN molecule", by R. SCHMID, L. GERÖ and J. ZEMPLÉN.

"Oxide-coated cathodes. Part I. Particle-size and thermionic emission", by M. BENJAMIN, Ph.D., R. J. HUCK and R. O. JENKINS, Ph.D.

"An x-ray study of the superlattice in certain alloys", by E. A. OWEN, M.A., Sc.D. and I. G. EDMUNDS, M.Sc., Ph.D.

"On the emission spectrum of $SiCl_2$ and $SnCl_2$ ", by R. K. ASUNDI, S. M. KARIM and R. SAMUEL.

11 March 1938

Annual General Meeting

The minutes of the previous Annual General Meeting were read and accepted as correct.

The reports of the Council and Hon. Treasurer and the accounts were adopted.

The Officers and Council for 1938-9 and the Auditors were elected.

Votes of thanks were accorded to the retiring Officers and Council and to the Governors of the Imperial College of Science and Technology.

Ordinary Meeting

The following were elected to Fellowship of the Society: R. N. Das, F. G. A. Haegele, B. H. Wilsdon.

A demonstration of some effects of radiation on liquids and gels was given by F. L. HOPWOOD, D.Sc., F.Inst.P. and J. T. PHILLIPS.

The following paper was read:

"A new form of frequency and time standard", by L. ESSEN, B.Sc.

The following papers were read in title:

"The acoustical conductivity of orifices", by N. W. ROBINSON, A.R.C.S., B.Sc., Ph.D.

"The relative luminosity of radiation at wave-lengths 5780 and 5461 Å. for the average photometric observer", by J. S. PRESTON, M.A., A.M.I.E.E., F.Inst.P.

"The fundamental unit of electric charge", by H. T. FLINT, D.Sc., Ph.D. and W. WILSON, D.Sc., Ph.D., F.R.S.

"A simple 'scale-of-two' counter", by H. ALFVÉN.

25 March 1938

The following were elected to Fellowship of the Society: Gordon Owen Baines, Walter Charles Gee.

A demonstration of the phenomenon of beats was given by D. A. RICHARDS, A.R.C.S., M.Sc.

The following paper was read:

"Elastic properties of sodium wires between -183° and 90° C." by R. H. V. M. DAWTON, B.Sc.

The following papers were read in title:

"The purification and magnetic properties of mercury", by L. F. BATES, D.Sc., Ph.D., F.Inst.P. and C. J. W. BAKER, B.Sc.

"The frequency of vibration of molecules in liquids and its relation to viscosity", by D. B. MACLEOD, M.A., D.Sc.

9 April 1938

A demonstration of molecular models of dielectrics was given by L. HARTSHORN, D.Sc.

The following papers were read:

"The propagation of supersonics in capillary tubes", by J. MAY, M.Sc.

"The motion of a mercury index in a capillary tube", by G. D. YARNOLD, M.A., D.Phil.

The following paper was read in title:

"The crystal structure of cadmium-indium alloys rich in indium", by W. BETTERIDGE, Ph.D.

13 May 1938

S. R. Rao was elected to Fellowship of the Society.

The President announced that Council had elected Philip Charles Bowes to Student Membership of the Society.

The Fifteenth Duddell Medal was presented to Professor H. GEIGER.

The Medallist gave a short account of recent results obtained with his counters on the multiplicative nature of shower formation.

The following paper was read:

"A simple type of helium cryostat", by J. G. DAUNT and K. MENDELSSOHN.
With demonstration.

The following papers were read in title:

"Attenuation and group retardation in the ionosphere", by G. MILLINGTON.

"An x-ray study of lattice distortion in metals. Part I. Intensity and line-width measurements of lattice distortion in rhodium", by G. W. BRINDLEY and P. RIDLEY.

27 May 1938

The following were elected to Fellowship of the Society: William Phelps Allis, Norman Frederick Astbury, James Albert Darbyshire, Niraj Nath Das Gupta, Claude Hurst, K. A. Selliah, William Alfred Wooster, Douglas Percy McKeon (transfer from Student).

A demonstration entitled "Roberval's enigma and its application to weighing mechanisms" was given by W. A. BENTON, F.C.S.

The following paper was read, followed by an informal discussion on Probability:

"A problem in coin-tosses", by S. R. SAVUR, M.A.

The following papers were read in title:

"Intensity of γ -radiation produced by slow neutrons", by R. D. HILL, M.Sc., and A. A. TOWNSEND, M.Sc.

"Thermionic emission from carbon", by A. L. REIMANN.

2 June 1938

Meeting held in the rooms of the Royal Society, Burlington House, London, W. 1 (by kind permission of the President and Council).

The following papers were read:

"Colour sensations produced by ultra-violet light", by A. G. GAYDON, Ph.D., A.Inst.P.

"The flashing character of aerodrome floodlight beacons", by W. M. HAMPTON, Ph.D., F.Inst.P. and J. G. HOLMES, A.R.C.S., B.Sc., F.Inst.P.

"Anomalous trichromatism and its relation to normal trichromatism", by J. H. NELSON, A.R.C.S., B.Sc., A.Inst.P.

10 June 1938

A demonstration of rhodium plating was given by A. W. SCOTT, A.C.G.I., F.I.C.

The following papers were read:

"A method of measuring self-inductance at radio frequencies", by ALBERT CAMPBELL, M.A.

"Secondary-electron emission of nickel, cobalt and iron as a function of temperature", by L. R. G. TRELOAR, B.Sc., F.Inst.P. and D. H. LANDON, B.Sc.

The following papers were read in title:

"The specific heat of nickel from 100° C. to 600° C.", by C. SYKES, D.Sc. and H. WILKINSON, Ph.D.

"The prediction of transmission phenomena at oblique incidence from ionospheric measurements at vertical incidence", by G. MILLINGTON.

"x-ray investigation of atomic vibrations in magnesium between 86° and 293° absolute", by G. W. BRINDLEY, M.Sc., Ph.D. and P. RIDLEY, B.Sc.

24 June 1938

The President announced that Council had elected K. B. S. Wilder to Student Membership of the Society.

The following demonstration was given:

"A low voltage cathode ray tube for visual demonstration of electron diffraction", by J. A. DARBYSHIRE, M.Sc., Ph.D.

The following papers were read:

"The dissipation of energy by a pendulum swinging in air", by E. C. ATKINSON, M.A.

"The amplitude deviation of rate of a pendulum: a second experiment", by E. C. ATKINSON, M.A.

The following papers were read in title:

"Diffraction of electrons by oxide-coated cathodes", by J. A. DARBYSHIRE, M.Sc., Ph.D.

"Heat-conduction in a medium having thermal properties depending on temperature", by M. R. HOPKINS.

"Measurements of the critical frequency of wireless waves reflected obliquely from the ionosphere", by F. T. FARMER, Ph.D., C. B. CHILDS, Ph.D. and A. COWIE, B.Sc.

"The nuclear magnetic moment of copper", by S. TOLANSKY, Ph.D. and G. O. FORESTER, B.Sc.

"An investigation of cosmic-ray showers produced under thirty metres of clay", by J. D. CRAWSHAW, M.Sc.

"Rotational analysis of the ultra-violet band system of germanium monoxide", by A. K. SEN GUPTA, M.Sc.

"The principal paramagnetic susceptibilities of potassium ferricyanide at low temperatures", by L. C. JACKSON, M.Sc., Ph.D.

REPORT OF THE COUNCIL FOR THE YEAR ENDING 28 FEBRUARY 1938

ANNUAL GENERAL MEETING

AN annual general meeting was held at the Imperial College of Science and Technology on 12 March 1937, for the presentation and adoption of the Reports of the Council and the Honorary Treasurer and for the election of Officers and Council.

SCIENCE MEETINGS

Seventeen science meetings were held during the period under review. At three of these meetings the Guthrie Lecture, the Thomas Young Oration and the Presidential Address were delivered, the other fourteen being occupied by the presentation and discussion of demonstrations and papers. Fifteen demonstrations were given, 30 papers were read by authors, and 34 papers were read in title only.

Fourteen of the meetings were held in the Physics Department of the Imperial College, by kind permission of the Rector and Governing Body and Professor G. P. Thomson.

One meeting was held on 26 November 1937 at the London (R.F.H.) School of Medicine for Women, Hunter Street, W.C.1, by kind invitation of the School Council and Miss M. D. Waller. Before and after the meeting, exhibits were on view in the Physics department and additional demonstrations were given by Miss Waller, Dr W. A. Leyshon and other members of the Physics staff, who also entertained Fellows and guests to tea.

For optical subjects alone, two evening meetings were held, one for papers on 3 June 1937, in the rooms of the Royal Society, by kind permission of the President and Council, and one for the Thomas Young Oration on 9 December 1937, at the Royal Institution, Albemarle Street, W.1, by kind permission of the Managers. One of the afternoon meetings at the Imperial College, 28 May 1937, also was devoted to demonstrations and papers on optical subjects only.

SUMMER MEETING AT GREENWICH

A visit was paid on 26 June 1937 to the Fuel Research Station, East Greenwich, by kind invitation of the Director, Dr F. S. Sinnatt. An introductory address by Dr Sinnatt was followed by a tour of the laboratories where many demonstrations were given by members of the research staff.

Lunch and tea were taken at the National Maritime Museum, Greenwich; and a tour of the museum was made during the afternoon, after an explanatory address by the officer-of-the-day.

CONFERENCE AT BRISTOL

By the kind invitation of Professor A. M. Tyndall, meetings took place at the H. H. Wills Physical Laboratory of the University of Bristol during the four days 13-16 July 1937, when a Conference on the Conduction of Electricity in Solids was held under the joint auspices of the Society and the University of Bristol. The papers read and discussed at this conference were published in an extra part of Volume 49 of the *Proceedings of the Physical Society*.

GUTHRIE LECTURE

The twenty-second Guthrie Lecture was delivered on 22 October 1937 at the Imperial College by Dr C. C. Paterson, who took as his subject "The Appraisalment of Lighting".

THOMAS YOUNG ORATION

At the Royal Institution on 9 December 1937, Dr R. J. Lythgoe delivered the tenth Thomas Young Oration on "The Structure of the Retina and the Role of its Visual Purple".

PRESIDENTIAL ADDRESS

The retiring President, Mr T. Smith, delivered his Address to the Society on 25 February 1938 at the Imperial College, the subject being "Vision through Optical Instruments".

DUDELL MEDAL

The fourteenth Duddell Medal, the award of which was announced in the previous report of the Council, was presented on 9 July 1937 to Professor W. G. Cady of the Wesleyan University, Middletown, Connecticut, U.S.A., for his work on piezo-electric oscillators and resonators as standards of time and frequency.

The Council has awarded the fifteenth Duddell Medal to Professor Hans Geiger, in recognition of his invention and subsequent improvement of his counters.

HERBERT SPENCER BEQUEST

Research Grants

During the period under review, the Council has made the first grants for research in physical science by Fellows of the Society. Five applications for grants were received and considered by the Council, and three grants were made, namely:

- (i) To Dr William H. Taylor, College of Technology, Manchester, for a quartz monochromator to be used in further investigations on the optical properties of metals.
- (ii) To Dr Dorothy M. Wrinch, Lady Margaret Hall, Oxford, for the construction of atomic models of insulin and related molecules.
- (iii) To Professor Herbert Dingle, Imperial College, for the purchase of lithium fluoride and the construction of a vacuum Littrow spectrograph with an optical train of this material.

Purchase of Radium

The Council has decided upon the purchase of 100 milligrams of radium in the form of the sulphate mixed with beryllium to serve as a neutron source. It is intended to loan this radium to Fellows of the Society for purposes of physical research. An application by Professor G. P. Thomson for the loan of it has been approved.

Furnishing of Council Room

The Council Room has been suitably furnished with tables, chairs and carpet. The photographs of the past Presidents of the Society since its foundation have been reframed.

PROGRESS REPORTS

Volume IV, which was recently published, is as comprehensive in scope as the three preceding volumes. The sales of Volume III have been highly satisfactory. The stock of copies of Volume II is almost exhausted and no copies of Volume I are available. The Council has decided that a number of copies of Volumes I and II offered for sale in good condition shall be repurchased by the Society.

ANNUAL EXHIBITION

The Twenty-eighth Annual Exhibition of Scientific Instruments and Apparatus was held on 4, 5 and 6 January 1938 at the Imperial College, by the courtesy of the Governing Body. The attendance during the three days was about 8500.

Seventy-seven firms exhibited their products in the Trade Section; in addition three firms displayed technical literature. The Research and Educational Section was nearly double that of previous years and contained contributions from thirty-seven University laboratories, research associations, Government and industrial laboratories, and private individuals. As in previous years, an Apprentices' and Learners' Competition in craftsmanship and draughtsmanship was held in conjunction with the exhibition, and the work entered for the competition was on view. The prizes and certificates awarded in the competition were presented to successful candidates at the meeting on 28 January 1938.

The following discourses were delivered during the exhibition:

"The Mechanical Amplification of Small Displacements", by Professor A. F. C. Pollard.

"Diving in Deep Water and Shallow", by Captain G. C. C. Damant.

As in previous years, permission was given to the Institute of Physics to publish these discourses in the February number of the *Journal of Scientific Instruments*.

REPRESENTATION OF THE SOCIETY

The Physical Society has been represented on other bodies as follows:

British National Committee for Physics: Mr T. Smith, Mr J. H. Awbery, Professor A. M. Tyndall.

British National Committee for Scientific Radio: Professor E. V. Appleton, Professor L. S. Palmer.

Committee of Management of Science Abstracts: Professor A. Ferguson, Dr D. Owen, Mr J. H. Awbery, Dr W. Jevons.

Board of the Institute of Physics: Dr D. Owen, Dr A. B. Wood.

Joint Committee on Symbols for Thermodynamics: Professor A. Ferguson, Mr J. H. Awbery, Professor A. C. Egerton, Professor G. I. Finch.

British Standards Institution Committee on Optical Projection Apparatus: Professor A. F. C. Pollard, Dr R. S. Clay.

Joint Deputation to the Postmaster General regarding the Suppression of Electrical Interference with Radio: Professor G. I. Finch, Professor E. V. Appleton, Dr D. Owen.

The Society has also been represented at the following functions:

Centenary Celebrations of the University of Durham, 1 and 2 July 1937: Mr T. Smith.

International Congress for Short Waves in Physics, Biology and Medicine, Vienna, 12-17 July 1937: Mr L. V. Kahn-Rein.

International Meeting of Physics, Chemistry and Biology, held in connexion with the Paris Exhibition: 30 September-9 October 1937: Dr H. Shaw.

Celebrations in honour of Professor Charles Fabry on the completion of fifty years of research and teaching, Paris, 3 December 1937: Professor G. Boutry.

AGREEMENT WITH THE INSTITUTE OF PHYSICS

The agreement with the Institute of Physics which expired on 31 December 1937 has been renewed for a further period of three years as from 1 January 1938.

Report of Council

OBITUARY

The Council records with deep regret the deaths of the following Fellows: Dr J. R. Airey, Professor H. E. Armstrong, Mr P. E. Belas, Dr W. N. Bond, Dr A. S. Burgess, Mr W. T. Clough, Mr C. W. S. Crawley, Mr R. Curry, Mr W. B. Ferguson, Mr J. Fleming, Professor A. Griffiths, Professor T. Mather, Professor L. Natanson, Lord Rutherford of Nelson, Mr K. Sunayama, Professor S. Young.

At the funeral of Lord Rutherford in Westminster Abbey, the Society was represented by the President and members of the Council.

MEMBERSHIP ROLL AT 31 DECEMBER 1937

	Total 31 Dec. 1936	Changes during 1937	Total 31 Dec. 1937
Honorary Fellows	11	—	11
Honorary Fellows (Optical Society)	7	—	7
Ex-officio Fellows	4	—	4
Ordinary Fellows	945	Elected 28 Student transfers <u>4</u> 32 Deceased 16 Resigned or lapsed <u>21</u> 37 Net change 5	940
Students	86	Elected 12 Transferred 4 Resigned or lapsed <u>15</u> 19 Net change 7	79
Total Membership	1053	Net decrease 12	1041

REPORT OF THE HONORARY TREASURER FOR THE YEAR ENDED 31 DECEMBER 1937

THE accounts show an excess of income over expenditure amounting to £92. 12s. 10d., which is considered satisfactory.

The publication of the Annual Reports on Progress in Physics continues without involving any charge on the general funds.

During the year the Council provisionally allocated the following amounts from the Herbert Spencer Bequest:

For Joint Library purposes	£300
For Loan for Research purposes:	
Radium, approximately	£410
Quartz Monochromator	£150
Models of Insulin and other molecules	£25

The Finance Committee recommends that the balance of the Optical Convention (1926) Trust Account, amounting to £51. 3s. 2d., be transferred to the General Fund in due course, with the understanding that in the event of another Optical Convention being held, the Council of the day be recommended to grant a sum of at least £60 towards the expenses.

No change has been made in the Society's investments. These have been valued at market prices on 31 December 1937, through the courtesy of the Manager of the Charing Cross Branch of the Westminster Bank.

(Signed) ROBERT W. PAUL
Honorary Treasurer

18 February 1938.

INCOME AND EXPENDITURE ACCOUNT FOR THE YEAR ENDED 31 DECEMBER 1937

1936			1937			1938			1939			1940			1941			1942		
£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.	£	s.	d.
EXPENDITURE																				
To																				
"Science Abstracts"																				
Normal Publications:																				
"Proceedings" and Exhibition Catalogue																				
Notices																				
Editorial and General Expenses																				
Special Publications:																				
"Reports on Progress in Physics" (Vol. III)																				
Postage on Normal Publications and General Correspondence																				
Expenses at Meetings																				
Periodicals and Library																				
Institute of Physics:																				
Clerical Assistance and Office Expenses																				
Electricity, Labour and Sundries in connexion with Exhibition																				
Summer Visit																				
Sundry Expenses																				
Honarium to Lecturer																				
Balance, being excess of Income over Expenditure, carried forward to Accumulated Fund.																				
1936																				
1937																				
1938																				
1939																				
1940																				
1941																				
1942																				
£5252 11 3																				

* Seventy-nine Fellows paid reduced subscriptions by the arrangement with the Institute of Physics, the total rebate being £31. 2s. 0d.

† Voluntary subscriptions are subscriptions paid by Fellows who compounded for the low sum of £10.

BALANCE SHEET AS ON 3 DECEMBER 1937

LIABILITIES				ASSETS				
£	s.	d.	£	s.	d.	£	s.	d.
<i>Surplus Creditors</i>				<i>Investments at Market Value on 31 Dec.</i>				
<i>Life Compositions:</i>				£2100 Consolidated Stock 2½ %				556 0 0
As on 31 December 1936				£1000 War Loan 3½ % Inscribed "A"				015 0 0
<i>Add</i> Payment during year				£750 War Loan 3½ % Registered				760 0 0
				£650 Funding Loan 4 %				780 0 0
				£500 India 3½ % Stock				465 0 0
<i>Less</i> Transfer to Income and Ex-				£400 Lancaster Corporation 3 %				376 0 0
penditure Account of amount				£399 London Midland and Scottish				
paid by Fellows now deceased				Debiture Stock				416 0 0
<i>Subscriptions paid in advance:</i>				£1000 London Midland and Scottish F				
Members				ilway 4 %				820 0 0
Publications				Preference Stock				515 0 0
				£500 London and North Eastern Railway 4 % De-				187 0 0
				biture Stock				261 0 0
				£150 Southern Railway 5 % Debiture Stock				87 0 0
				£300 Southern Railway Preferred Ordinary Stock				406 0 0
				£442 Southern Railway Deferred Ordinary Stock				
				£400 War Loan 3½ % Inscribed "B" Account				
								7504
<i>Accumulated Fund:</i>				<i>Dividends due from Investments</i>				38
As on 31 December 1936				<i>Inland Revenue—Income Tax claimed for 1937</i>				30
<i>Less</i> Decrease in value of Invest-				<i>Subscriptions due</i>				42
ments				<i>Sundry Debtors</i>				177
				<i>Cash at Bank: Current</i>				1 11
				<i>Cash on Deposit</i>				0 10
				<i>Cash in hand</i>				1 1
								517
<i>Add</i> Balance of Income and Ex-								
penditure Account								
<i>A. W. Scott Bequest</i>								

Stock of publications on 31 December 1937. At				£
Honorary Treasurer's valuation				4s. d.

NOTE: These accounts do not include the usual liabilities incurred in 1937 in respect of publications to be issued in 1937, amounting to approximately £382.

We have audited the above Balance Sheet and have obtained all the information and explanations we have required. We have verified the Investments. In our opinion such Balance Sheet is properly drawn up so as to exhibit a true and correct view of the affairs of the Society's affairs according to our information and the explanations given to us and as shown by the books of the Society.

SPENCER HOUSE, SOUTH PLAC, E.C. 2
8 March 1938.

ROBERT W. PAUL, *Honorary Treasurer.*

KNOX, CROPPER & Co.,
Charter

LIFE COMPOSITION FUND ON 31 DECEMBER 1937

	£	s.	d.
41 Fellows paid £10	.	.	.
1 Fellow paid £15	.	.	.
15 Fellows paid £21	.	.	.
28 Fellows paid £31. 10s.	.	.	.
	£	1464	10 0

SPECIAL FUNDS

W. F. STANLEY TRUST FUND

Carried to Balance Sheet	£	s.	d.	£300 Southern Railway Preferred Ordinary Stock	£	s.	d.
	848	0	0		261	0	0
				£442 Southern Railway Deferred Ordinary Stock	87	0	0
	£848	0	0		£848	0	0

DUDELL MEMORIAL TRUST FUND

CAPITAL

Carried to Balance Sheet	£	s.	d.	£400 War Loan 3½% Inscribed "B" Account	£	s.	d.
	406	0	0		406	0	0

REVENUE

Engraving medal	£	s.	d.	Balance on 31 December 1936	£	s.	d.
Honorarium to Medallist	2	2	0	Interest	9	0	9
Balance carried to Balance Sheet	5	18	9		14	0	0
	£23	0	9		£23	0	9

OPTICAL CONVENTION, 1926, TRUST ACCOUNT

Balance carried to Balance Sheet	£	s.	d.	Balance on 31 December 1936	£	s.	d.
	51	3	2	Sales of Publications	49	1	8
				Sundries	1	10	0
	£51	3	2		11	6	
					£51	3	2

A. W. SCOTT BEQUEST

Expenses in connexion with Library	£	s.	d.	Balance on 31 December 1936	£	s.	d.
Balance carried to Balance Sheet	1	3	4		174	15	3
	173	11	11				
	£174	15	3		£174	15	3

"SPECIAL REPORTS ON PHYSICS" ACCOUNT

Balance carried to Balance Sheet	£	s.	d.	Balance on 31 December 1936	£	s.	d.
	83	1	0		83	1	0

HERBERT SPENCER LEGACY

Special Library Expenses	£	s.	d.	Balance on 31 December 1936	£	s.	d.
Furniture for Council Room	87	15	6		1241	0	0
Balance carried to Balance Sheet	123	16	2				
	1029	8	4				
	£1241	0	0		£1241	0	0

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

VOL. 50, PART I

January 1, 1938

No. 277

THE ELECTRIC CHARGES ON SINGLE RAINDROPS AND SNOWFLAKES

BY J. ALAN CHALMERS, M.A., PH.D. (Cantab.),
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AND

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Pemberton Research Fellow, University College, Durham

Communicated by Dr Bruce Chalmers, 10 July 1937. Read 8 October, 1937

ABSTRACT. An account is given of 16 months' observations on the charges of individual raindrops and snowflakes. The results show an excess of positively charged drops and of total positive charge, except for storm rain. The average charge per drop is greater in the case of negative than of positive raindrops, but the reverse holds for snowflakes. Observations were also made of the sequences of drops of one sign, of the relative proportions of drops of the two signs in different parts of a single rainfall and of the distribution in magnitude of the charges. A brief discussion is given of the problems of the origin of the charges on rain.

§ 1. INTRODUCTION

OBSERVATIONS of the charges carried by raindrops and other forms of atmospheric precipitation can contribute to the discussion of two of the main problems of atmospheric electricity, namely, the problem of the maintenance of the negative charge on the earth's surface in fine weather, and the problem of the origins of the electrical phenomena of stormy conditions.

The total vertical current due to precipitation must play a part in what Wormell⁽²⁴⁾ has termed the "electrical balance sheet" of the earth. If the precipitation current brings down to the earth a positive charge, then this must be added to the effect of the fine-weather current and both must be balanced by some other process or processes; on the other hand, if a negative charge is brought down, it will help to neutralize the fine-weather current. It must be pointed out that any secondary effects occurring during the rainfall should be included in the vertical current; for example, if splashing causes a separation of charge and some of this is carried upwards and does not reach the earth, then there will be a resultant vertical current differing from that carried by the actual raindrops; in the same way the ionic

conduction current should be included in the total vertical current in bad weather conditions, particularly as this might have a greater value than in fine weather, owing to extra sources of ionization.

It is possible that measurements of the charges on raindrops can give some information as to the processes giving rise to electrical effects in clouds, for it seems generally agreed that water-drops must be the agency by which the charges in storm clouds are built up. In this connexion, it is clearly more useful to measure the charges on individual drops than to obtain merely the average for a large number of drops.

The majority of the measurements of the charges on rain have taken the form of a compromise between the two types of measurement discussed above. In the experiments of Elster and Geitel⁽⁸⁾, Gerdien⁽⁹⁾, Kähler⁽¹³⁾, Simpson⁽²¹⁾, Benndorf⁽⁵⁾, Baldit^(1,2,3), McClelland and Nolan^(17,18), Berndt⁽⁶⁾, Schindelbauer⁽¹⁰⁾, McClelland and Gilmour⁽¹⁶⁾, Miss Marwick⁽¹⁵⁾ and Banerji⁽⁴⁾, a receiver was used which was shielded to prevent rain splashing into it from outside, and to avoid any effects due to field-changes; care was also taken to prevent effects due to splashing inside the receiver. In all these experiments, measurements were made of the charge brought down by the number of drops arriving on a definite area in a certain time; or, in some cases, by the number of drops in a given volume of rain. Yet most of the observers have discussed their results in connexion with the total vertical current during the precipitation, neglecting the ionic current and any secondary processes such as splashing effects.

Weiss⁽²²⁾ used a wire brush to receive the drops, but it was found that there were effects due to point discharges and the method was of little value. Kohlrausch⁽¹⁴⁾ shielded the brush from the earth's field, and thus his observations come into the same category as those considered above.

Herath⁽¹²⁾ has used a large area of cloth, completely exposed, as a receiver, and hence some, at least, of the secondary processes can come into operation. Schonland⁽²⁰⁾ also made some observations with a completely exposed test plate.

Gschwend⁽¹⁰⁾ alone has made observations on the charges carried by individual drops, and it is clear that it is only such observations that can give accurate information about the drops. In the usual method of measurement, all that can be obtained is the average for a large number of drops, and it is not even possible to tell whether or not the charges on the drops are all of the same sign. Gschwend has discussed the fact that the average current for a number of drops is much smaller than the instantaneous current, and the same applies to the average and single charges.

Furthermore, previous observers, who have shielded their receivers, have thereby excluded any rain falling at a considerable angle to the vertical; in most cases, rain falling more obliquely than at 40° to the vertical cannot possibly be recorded. Thus, in driving rain, no observations have been possible, and consequently a fair sample of rain has not been obtained.

Most of the observers have made, in addition, simultaneous observations of other relevant quantities, e.g. potential-gradient, rate of rainfall and size of drops,

but few relations have been found between these quantities and the charges on the rain.

Since the different observers referred to above have found results which show marked divergences, it was considered desirable to carry out further observations by the method of Gschwend⁽¹⁰⁾, in order to obtain further information about the charges on individual drops. In view of Gschwend's result that there is no definite relation between the size and charge of a drop, it was decided to concentrate on the measurement of the charges of as many as possible of the drops falling on one particular area. To avoid missing the driving rain, the apparatus was arranged to receive as much as possible of the rain, no matter at what angle it was travelling.

§ 2. THE APPARATUS

The vessel used for the reception of raindrops is of metal and of the shape shown in figure 1. It has a height of 16 cm., a maximum diameter of 7.3 cm., and an orifice 4 cm. in diameter. It is insulated on sulphur, which is kept warm and dry by means of a heating coil. The receiver and insulator are contained in a metal vessel 16 cm. in diameter and 20 cm. high with a lid of the shape shown in figure 1;

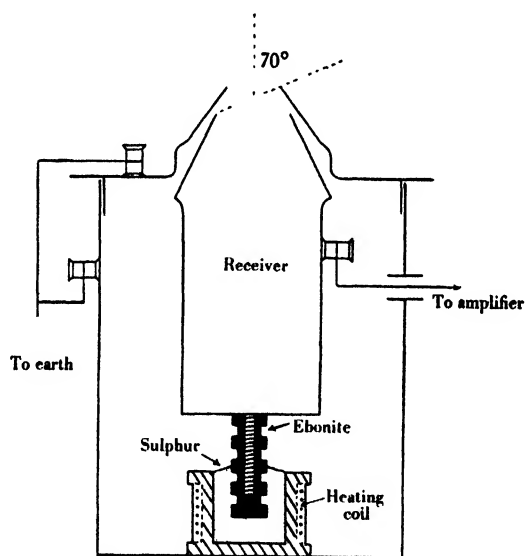


Figure 1.

the frustum-shaped portion of the lid fits closely over the correspondingly shaped top of the receiver. This outer container and lid are connected to earth, and so the receiver is protected almost completely from variations in the earth's field. The effective aperture of the receiver is reduced by the lid to a diameter of 2.9 cm. or an area of 6.6 cm², and the shape and dimensions of the apparatus show that drops at an angle as great as 70° to the vertical can enter the receiver.

The arrangement is set up on the flat roof of the Science Laboratories at Durham as far away as possible from any elevated objects. From the receiver, a shielded cable passes through a hole in the roof into the room below which contains the measuring-instrument. The latter, described in detail elsewhere by Chalmers and Pasquill⁽⁷⁾, consists of a two-stage valve bridge amplifier used in conjunction with a dead-beat mirror galvanometer, and has a limit of accuracy of the order of 10^{-4} e.s.u. of charge.

Owing to the comparatively low resistance of the amplifier, there are no serious insulation difficulties. The two principal possibilities of error are concerned with effects of splashing and of sudden changes in the vertical electric field of the atmosphere. With regard to splashing, there are two aspects to be considered; the first is the possibility of the splashing out of drops entering the receiver, and the second the possibility of splashing in from outside. The first possibility is minimized by the shape of the receiver and an experimental test was performed; drops carrying a definite charge were allowed to fall from different heights, and it was found that no alteration occurred in the readings obtained even when splashing did take place in the receiver; thus the assumption that there would be no splashing out was verified. The second possibility was considered by observing the apparatus during rainfall; it was found that only in the very heaviest of rain did drops splash from the flat portion of the lid into the orifice, and even then such occasions were rare and the effect can be neglected in comparison with the large number of heavily charged drops generally observed in heavy rain.

As the receiver is slightly exposed to the earth's field at the orifice, an experimental test was performed which showed that a sudden field-change of about 6000 v. per metre in the proximity of the apparatus would be accompanied by an apparent charge of 2×10^{-3} e.s.u. on the receiver. Since such a field-change would only occur in a close thunderstorm, the effect would probably be negligible in comparison with the effects of the drops and would be much less frequent. Since the charges on the raindrops are measured instantaneously, there is no possibility of error due to any electrical effects which may be due to evaporation of the drops (cf. Gunn⁽¹¹⁾), the latter process being comparatively slow.

In practice, visual observations were made of the galvanometer deflections and, consequently, often only part of a period of rainfall could be examined. In particular, it was not always possible to commence observations at the beginning of the rain. During observation, the deflection corresponding to each drop was noted and a calibration was performed periodically.

Occasionally, abnormally large deflections were observed, and these could be recognized as abnormal in character, since they did not give the usual clear kick; a rough experimental test showed that these deflections were due to drops accidentally short-circuiting the space between the receiver and the lid above it; they were therefore neglected.

In very fine rain it was not found possible to make observations, probably owing to the sensitivity of the amplifier being insufficient to measure the very small charges concerned.

§ 3. EXPERIMENTAL RESULTS

From the observations performed, it has been found possible to obtain a number of general results for the whole year 1936 and the first four months of 1937, and for a seasonal variation during the period. These points have been dealt with first in the following presentation of the experimental results.

Table 1. Seasonal variation

Season	Total positive (e.s.u.)	Total negative (e.s.u.)	Ratio + ve/- ve	Surplus	Duration (min.)	Mean current (10^{-16} amp./cm ²)
*Winter, 1936	6.81	3.36	2.03	+ 3.45	1478	+ 1.9
Spring	10.82	8.65	1.25	+ 2.17	977	+ 1.8
Summer	3.63	5.54	0.65	- 1.91	612	- 2.6
Autumn	3.07	2.18	1.41	+ 0.89	493	+ 1.5
*Winter, 1937	8.73	5.79	1.51	+ 2.94	676	+ 3.6

* "Winter" is taken as the three months January, February and March, with the other seasons to correspond.

For the convenience of a more detailed analysis, the precipitations observed have been divided into the following groups: (i) continuous fine rain, (ii) continuous heavy rain, (iii) continuous driving rain, (iv) showers, (v) squall rain, (vi) storm rain, (vii) snow, (viii) sleet, and (ix) hail. No actual thunderstorms occurred during the observations, but "storm rain" designates rain during which the conditions approached those generally associated with thunderstorms.

To avoid confusion in terms, the word *rainfall* is adopted to signify any period of rain, of any type, during which or during part of which observations were performed. Often it was not possible to make observations continuously throughout the whole period of a rainfall, but the different periods of observation have been combined to give results for the whole rainfall.

For each separate rainfall the following data were obtained: (1) The duration of the observations, (2) the total number of drops of each sign, (3) the total charge of each sign, (4) the number of changes of sign during the rainfall, (5) the *course* of the rainfall (i.e. whether or not one sign predominated in any one part of the rainfall), and (6) the distribution in magnitude of the charges on the individual drops received during the rainfall.

From the first four sets of data the following results are obtained, and the values of these for each type of precipitation are tabulated in table 2: (a) the mean current per cm², (b) the ratio of total positive to total negative charge, (c) the number of positively and negatively charged drops, (d) the average positive and negative charge per drop, (e) the average number of sign-changes per minute, (f) the average sequence of positive and of negative drops.

The first two of these groups of results have been obtained by other workers by means of the more usual type of observations and here are not considered of paramount importance; they are inserted merely for the purpose of comparison with earlier results.

In table 3 the different rainfalls have been classified according to their courses and the sequences of positive and negative charges. In figure 2 the course of one example of a rainfall is considered in detail.

Table 2. Summary of results for all types of precipitation

	Con- tinuous fine rain	Con- tinuous heavy rain	Con- tinuous driving rain	Showers	Squall rain	Storm rain	All types of rain	Snow	Sleet	Hail	Snow, etc.
No. of +ve rainfalls	13	14	5	5	6	2	45	5	5	3	13
No. of -ve rainfalls	5	2	0	5	1	6	19	8	1	1	10
Mean current (10^{-18} amp./cm ²)	+0.9	+2.5	+0.9	+0.6	+2.2	-13.6	+1.0	+5.0	+1.5	+2.0	+3.2
Total +ve charge											
Total -ve charge	2.82	1.38	1.28	1.42	9.85	0.35	1.23	1.43	1.38	1.65	1.42
No. of +ve drops	1718	4828	1296	768	201	312	9123	883	921	167	1971
No. of -ve drops	489	2806	611	523	12	355	4796	1138	452	102	1692
Average +ve charge per drop (10^{-8} e.s.u.)	0.9	3.0	1.8	1.1	1.3	3.7	2.3	10.5	3.2	2.6	6.4
Average -ve charge per drop (10^{-8} e.s.u.)	1.1	3.7	3.0	1.2	2.3	9.2	3.5	5.7	4.7	2.6	5.3
Average no. of sign- changes per min.	0.6	1.8	1.3	1.4	0.1	1.6	1.3	1.1	0.8	1.0	1.0
Average +ve sequence	7	4	4	3	37	3	4	4	5	4	4
Average -ve sequence	2	2	2	2	2	4	2	5	2	3	4

Table 3. Classification of rainfalls according to courses and sequences

	Con- tinuous fine rain	Con- tinuous heavy rain	Con- tinuous driving rain	Showers	Squall rain	Storm rain	All types of rain	Snow	Sleet	Hail
Entirely +ve	3	0	0	1	5	0	9	0	1	1
+ve sequences and -ve singles	9	4	3	4	1	2	23	0	0	0
+ve sequences early -ve sequences later	2	5	0	1	0	1	9	1	0	0
Sequences of both signs	2	4	2	2	0	2	12	6	3	2
-ve sequences early +ve sequences later	0	3	0	1	0	0	4	3	1	1
-ve sequences and +ve singles	2	0	0	1	1	2	6	0	1	0
Entirely -ve	0	0	0	0	0	1	1	3	0	0

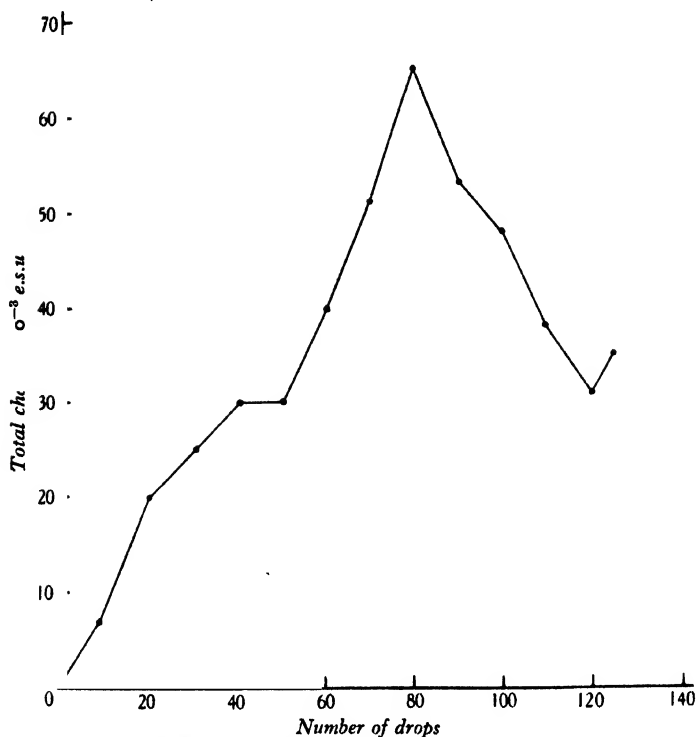


Figure 2. Example of a rainfall with positive sequences early and negative sequences later. For convenience the rainfall is divided into groups of 10 drops each. This rainfall was observed on 22 June, lasted about 40 min., and is classified as a shower.

Table 4. Distribution in magnitude of charges

Charges (10 ⁻⁹ e.s.u.)	Con- tinuous fine rain	Con- tinuous heavy rain	Con- tinuous driving rain	Showers	Squall rain	Storm rain	All types of rain	Snow	Sleet	Hail	Snow, sleet and hail
> +5	41	662	88	18	10	72	891	319	80	23	424
+4 to +5	10	102	26	1	0	10	149	15	8	1	24
+4 to +4	3	66	8	4	1	16	98	16	5	6	27
+3 to +4	6	145	14	3	2	15	185	21	12	6	39
+3 to +3	15	149	31	10	7	8	220	38	19	6	63
+2 to +3	22	240	36	19	5	13	335	43	15	3	61
+2 to +2	19	311	58	28	7	13	436	38	25	12	75
+1 to +2	50	409	64	49	6	32	610	59	47	10	116
+1 to +1	112	561	94	66	24	28	885	73	113	20	206
+ to +1	250	944	212	135	37	58	1636	102	148	32	282
+ to +	839	1150	515	305	79	42	2930	136	423	40	599
- to +	443	138	207	204	23	6	1021	42	56	10	108
- to -	261	545	170	270	2	12	1260	211	164	24	399
-1 to -	58	523	90	74	1	32	778	215	60	13	288
-1 to -1	25	394	60	35	5	15	534	99	48	6	153
-2 to -1	18	209	25	13	2	19	286	73	33	9	115
-2 to -2	3	195	39	9	0	32	278	67	13	15	95
-3 to -2	4	117	25	6	0	24	176	43	7	8	58
-3 to -3	1	99	26	3	0	6	135	34	15	6	55
-4 to -3	3	67	8	5	0	36	119	28	8	5	41
-4 to -4	4	56	5	3	1	17	86	27	9	0	36
-5 to -4	2	74	12	4	0	13	105	14	5	1	20
< -5	18	478	94	27	1	148	766	308	60	13	381

Table 4 shows the distribution in magnitude of the charges on the individual drops for the different types of precipitation. The total number of drops carrying average charges 0 ($-\frac{1}{4}$ to $+\frac{1}{4}$), $\pm\frac{1}{2}$ ($\frac{1}{4}$ to $\frac{3}{4}$), ± 1 ($\frac{3}{4}$ to $1\frac{1}{4}$), etc., up to ± 5 ($4\frac{3}{4}$ to $5\frac{1}{4}$) in units of 10^{-3} e.s.u. for all types of rain, and for snow, sleet and hail combined, are shown graphically in figure 3. It must be realized that, since the finest rain is not

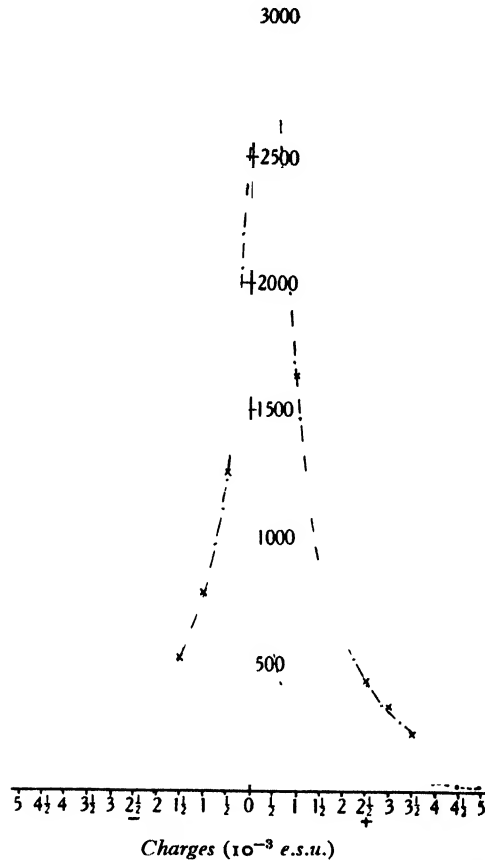


Figure 3. Distribution in magnitude of charges.

— all types of rain - - - - - snow, sleet and hail

observed and the limit of measurement is usually about 2×10^{-4} e.s.u., a large number of drops carrying charges from $-\frac{1}{4}$ to $+\frac{1}{4} \times 10^{-3}$ e.s.u. will have been missed, and consequently the centre portion of the curve can only be estimated.

Table 5. General results for the period

Total number of positively charged drops observed	...	11,094
Total number of negatively charged drops observed	...	6,488
Ratio of numbers of positive and negative drops	...	1.71
Total positive charge received (e.s.u.)	...	33.2
Total negative charge received (e.s.u.)	...	25.6
Ratio of total positive to total negative charge	...	1.30
Surplus of charge (e.s.u.)	...	7.6

With regard to seasonal variation, only one rainfall was observed in each April and none in August. Of the remaining months, only July showed a definite predominance of negative charge (with a mean current of -4.0×10^{-15} amp./cm²), November was slightly negative, while March 1936 and September were almost neutral, despite the large number of drops observed in the latter month. All other months showed a definite positive predominance. Table 1 was obtained by grouping the months into seasons.

§ 4. DISCUSSION OF THE GENERAL EXPERIMENTAL RESULTS AND COMPARISON WITH THOSE OBTAINED BY PREVIOUS OBSERVERS

(a) *Ratio of total positive to total negative charge.* The ratio of total positive to total negative charge is found to be 1.30, or, if we leave out snow, sleet and hail, 1.23. All previous workers except Elster and Geitel⁽⁸⁾, Gerdien⁽⁹⁾ and Banerji⁽⁴⁾ have found a positive-to-negative ratio greater than 1, but in actual magnitudes there is little agreement. Banerji⁽⁴⁾, observing only thunderstorms, at Bombay found a ratio of 0.85, Baldit^(1,2,3) at Puy-en-Velay in France found 1.36, Schindelhauer⁽¹⁹⁾ at Potsdam found 1.4, Gschwend⁽¹⁰⁾ at Freidberg in Switzerland 1.5, Simpson⁽²¹⁾ at Simla in India 3.2, Miss Marwick⁽¹⁵⁾ at Otago in New Zealand 3.2, McClelland and Nolan^(17,18) at Dublin 4.8, McClelland and Gilmour⁽¹⁶⁾ at Dublin 5.2, Herath⁽¹²⁾ at Kiel 15, and Schonland⁽²⁰⁾ in a few thunderstorms, in South Africa, 30.

Since the present observations have not included the finest rain, which McClelland and Nolan^(17,18) and McClelland and Gilmour⁽¹⁶⁾ found to be negative and Gschwend⁽¹⁰⁾ positive, the low value found for the ratio might be accounted for by accepting Gschwend's result. The divergence is still less surprising when one considers not only the effects of different climates, different predominating kinds of rain, different local conditions, different angles of reception, and different apertures, but also the method by which the ratio is obtained. In all cases except those of Gschwend and the present authors, the resultant charge only, either positive or negative, has been recorded for each definite interval or each definite volume of rain; consequently, an interval during which both positive and negative charges fall, with a predominance of positive, will be observed as positive only and will contribute only to the positive total. If, for example, the negative charges occur only for short intervals or only on small areas at once, then the observed positive-to-negative ratio would be increased by an increase of the time interval considered or of the area of the receiver. But in the present measurements and those of Gschwend, each drop is considered separately, and thus the ratio of positive to negative is less than if obtained from the other type of measurement. In illustration of this point, each rainfall can be considered as a whole, and the positive and negative surpluses can be added; this method gives a positive-to-negative ratio of 2.6.

(b) *Mean currents per cm²* The observations of Gerdien⁽⁹⁾, Kähler⁽¹³⁾ and Schindelhauer⁽¹⁹⁾ give the values shown in table 6.

Table 6. Average values of vertical currents (amp./cm²)

Ordinary rain	...	10^{-15}
Squall rain	...	10^{-18}
Thunder rain	...	10^{-14} to 10^{-18}

Whereas Gerdien found the current to be negative in each case, most of the later workers have found positive currents for ordinary rain and thunder rain, Simpson⁽²¹⁾, in particular, finding large positive currents for thunder rain, while Schindelhauer⁽¹⁹⁾ and Baldit^(1,2,3) frequently observed strong negative currents for squall rain.

The present observations gave a vertical current of the order of 10^{-15} amp./cm² for fine, heavy and driving rain and showers, and in the case of the heaviest rain the current has risen to 10^{-14} amp./cm² on occasions. Squall rain gave a positive current of small magnitude, in contrast to the large negative currents observed by Schindelhauer and Baldit. On the other hand, storm rain gave a negative current of the order of 10^{-14} amp./cm², in contrast to the large positive currents observed by Simpson⁽²¹⁾ and Schonland⁽²⁰⁾, but in general agreement with the negative surplus found for thunder rain by Banerji⁽⁴⁾. No currents have been observed to compare in magnitude with those previously observed, but this may be due to the absence of any very heavy rain.

(c) *Seasonal variation.* The present observations show a very marked seasonal variation, due principally to the negative charges on storm rain; the positive-to-negative ratio has a maximum value in winter and a minimum in summer. Schindelhauer⁽¹⁹⁾ found a maximum in winter and a minimum in spring, while McClelland and Nolan^(17,18), in a series of observations from October 1911 to May 1912, found the ratio to be greatest in spring. McClelland and Gilmour⁽¹⁶⁾ also found a negative excess in July, but a positive excess in August.

(d) *The positive-to-negative ratio for different types of precipitation.* The main points of interest lie in the very high ratio for squall rain and the very low ratio for storm rain. These are of special importance since Schindelhauer⁽¹⁹⁾ found a ratio less than unity for squall rain, Gschwend⁽¹⁰⁾ found 0.55, and Baldit's^(1,2,3) ratio was only 1.1. For storm rain in India, Simpson⁽²¹⁾ found a very high ratio (as did Schonland⁽²⁰⁾ in South Africa), but Banerji⁽⁴⁾ found a ratio of only 0.85; under conditions nearer to those of the present observations, McClelland and Gilmour⁽¹⁶⁾ found a ratio just over unity and Gschwend⁽¹⁰⁾ found 1.51. Such a wide variation can be attributed only to the differences in meteorological conditions.

Previous observers have disagreed as to the electrical charges on snow. Weiss⁽²²⁾, Simpson⁽²¹⁾, Gschwend⁽¹⁰⁾ and Miss Marwick⁽¹⁵⁾ found a positive excess, whereas Elster and Geitel⁽⁸⁾, Kähler⁽¹³⁾, Schindelhauer⁽¹⁹⁾, McClelland and Nolan^(17,18) and McClelland and Gilmour⁽¹⁶⁾ found a negative excess.

In the present observations, it was found that those snowfalls which consisted of large flakes were predominantly positive and those which consisted of small

flakes were predominantly negative; this is in agreement with the results obtained by McClelland and Nolan and by Gschwend. It is probable that the divergences quoted above may be ascribed to excesses of either type of flake.

Sleet and hail (most of the latter being in the form of soft hail) both give positive and negative ratios greater than unity, which is in agreement with all previous observers with the exception of Schindelbauer.

§ 5. DISCUSSION OF RESULTS PECULIAR TO THE PRESENT TYPE OF OBSERVATIONS

(a) *The individual drops.* The results can be compared with those of Gschwend⁽¹⁰⁾. The relative number of positive and negative drops is 1.71, as compared with Gschwend's value of 1.78 obtained mainly from observations of single drops at intervals. In the present work all types of precipitation, with the exception of storm rain and snow, show an excess of positive drops. In storm rain there is a slight excess of negative drops, while for snow there is a definite excess. Gschwend found an excess of positive drops in all types of precipitation except thunder rain, and in this he found approximately equal numbers of drops of both signs. However, his ratio of positive-to-negative drops for squall rain is less than in the present observations.

The mean charges per drop can be compared directly with those obtained by Gschwend. The values for all the different types of precipitation are given in table 2, but, for comparison with Gschwend, fine, heavy and driving rain and showers have been grouped together as "ordinary rain" in table 7. Since the finest rain has not been measured in the present work, agreement with Gschwend cannot be expected for ordinary rain.

Table 7. Mean charges per drop (10^{-8} e.s.u.)

	Gschwend		Present work	
	+ ve	- ve	+ ve	- ve
Ordinary rain	0.24	0.53	2.2	3.0
Squall rain	1.75	5.43	1.3	2.3
Thunder or storm rain	8.11	5.88	3.7	9.2
Continuous snow	0.09	0.06	10.5	5.7
Bursts of snow	5.64	4.78		

The most striking characteristic of the present observations is that for every type of rain the average negative charge per drop is greater than the average positive charge per drop. This agrees with the observations on ordinary and squall rain observed by Gschwend, but not with those on storm rain, possibly owing to the fact that no observations were made during actual thunderstorms. The present work agrees with that of Gschwend in finding approximately equal numbers of positive and negative drops during storm rain, but Gschwend obtained a positive excess due to the greater mean charge per drop on positive drops, while the reverse

holds in the present observations. The greatest charges obtained were during a snowfall and reached up to $+150 \times 10^{-3}$ e.s.u. and -110×10^{-3} e.s.u. No rain-drops were observed with charges greater than $\pm 90 \times 10^{-3}$ e.s.u.

For snow the results correspond except in that much of the snow observed might be considered more correctly as "continuous" rather than as "bursts".

(b) *Sign-changes and sequences.* Gschwend states that the most striking point emerging from continuous observations of the individual drops falling on a small area is the frequency of the changes of sign of the charges carried by the drops. He found that it was only in ordinary rain (*Landregen*) that drops carrying charges of one sign only fell on a surface of 12 cm^2 in 1 min. For fine rain he found 3 or 4 sign-changes per minute to occur frequently, while as many as 8 changes in half a minute were observed. In one thunderstorm, 60 drops fell in 3 min. and there were 38 sign-changes.

Although the reception area employed here was much less than (just over one half of) that used by Gschwend in the above cases, a comparison is possible. An analysis of the present observations shows that for all types of rain the average number of sign-changes per minute is slightly greater than unity. This appears small in comparison with Gschwend's values, but it is only an average, which is often exceeded. For example, in one storm shower lasting 9 min. there were 38 sign-changes, an average of 4 per minute; also in one rainfall of continuous heavy rain, the average number of sign-changes per minute was found to be 3; yet in parts of the rainfall there were whole minutes without any changes of sign, whereas in other parts as many as 12 sign-changes per minute were observed.

Bound up with this question of sign-changes is the question of sequences of one sign. There is one definite conclusion arising out of the observations, namely, that the sequences are more frequent than would be expected on pure chance. In some rainfalls, predominantly positive, the few negative drops are not, as might be expected, distributed at random among the positive drops, but there is a definite tendency for the negative drops to occur at nearly the same time, giving a negative sequence. This must be interpreted to mean, in the first place, that there is a process (or processes) for giving raindrops a negative charge, quite as definite and ordered as that for producing a positive charge on the drops; and, secondly, that there may be temporary, and perhaps local, conditions favouring the reception of drops of first one sign and then of the other. In this connexion an observation of Herath⁽¹²⁾ is interesting; he found that the infrequent negative currents often coincided with a lull in the rainfall.

(c) *The courses of the rainfalls.* The results in table 3 suggest that there are various types of rainfall, with different courses, and the particular course will be determined by the agencies responsible for the charges on the raindrops and the prevailing meteorological conditions.

The most striking feature of table 3 is the nine examples of rainfalls with sequences of positively charged drops early and sequences of negatively charged drops later. In some of the rainfalls classified as "sequences of both signs", the percentage of positive charge is greater in the earlier part of the rainfall than later.

Simpson⁽²¹⁾ in his first series of observations, found some indication of a similar result, but his later observations did not confirm this, and he finally concluded that there was no definite evidence that one sign predominated in any one part of a storm. McClelland and Nolan^(17,18) concluded that in some cases the occurrence of negative charge is associated with the latter part of a rainfall, but that this does not always hold. The present results agree with this conclusion, particularly in the case of continuous heavy rain.

(d) *The distribution in magnitude of the charges.* No previous observation has been able to give any result with which table 4 and figure 3 can be compared.

The general result of the analysis of the distribution is that we obtain a curve, figure 3, which is approximately symmetrical, with a maximum in the region of a small positive charge (about 0.3×10^{-3} e.s.u.). However, it would not be correct to imagine that the distribution is of the nature of an error function, for the results quoted above for the courses and sequences of sign show that in any one part of a rainfall we may have drops which fall mainly into one part of the distribution curve, while in another part of the rainfall, or in a separate rainfall may appear drops in another part of the curve. Moreover, in many of the separate rainfalls the distribution is far from symmetrical. This is true, in particular, of squall rain, storm rain and snow. Table 4 also shows that the spread of the distribution curves is greater in the more violent forms of rainfall, although it must be realized that this may possibly be due to the fact that more of the lightly charged drops might be missed in such cases.

It seems possible to reach the conclusion that, at any rate in ordinary rain, the charges on the drops are distributed symmetrically, and hence the distinction previously made (e.g. in the sequences) between positive and negative drops is not of great significance. In the more violent types of rain the distribution points do not fit so closely on a smooth curve, and it may be that factors operate which make the distribution more erratic; in particular may be noticed the steep fall on the negative side in the case of squall rain.

The preponderance of drops with small positive charges is related to the fact discussed above that the average positive charge is less than the average negative charge.

If the distribution curve is truly symmetrical, then we can estimate how many drops there are with charges from $-\frac{1}{4}$ to $+\frac{1}{4} \times 10^{-3}$ e.s.u. that have been missed by the present type of measurement; we see that the total should be about 2700, of which only 1021 were observed. It is interesting to note that the correction thus made to the average charges on positive and negative drops will still leave these considerably above the values obtained by Gschwend for ordinary rain (see table 7). Either Gschwend's large number of drops with small charges is incorrect, or else such drops must be additional to the distribution curve of figure 3, if this is kept as a symmetrical curve.

§ 6. GENERAL DISCUSSION OF RESULTS

It is not proposed to give, here, any attempt to account for the results that have been obtained, in terms of theories of the production of charges on water-drops. But it seems desirable to point out the significance of some of the results obtained from this and other work.

The general intermixing of positive and negative charges on raindrops suggests that one single process of separation of charge will not suffice to account for the results, but that it may be necessary to consider the drops to acquire their charges by at least two processes, which may be of different importance under different temporary and local conditions, giving rise to the sequences.

Interesting problems are raised in connexion with the question of the relation of the vertical potential gradient in the atmosphere to the charges on the raindrops; Benndorf⁽⁵⁾ and Gschwend⁽¹⁰⁾ state that often, but by no means always, the potential-gradient is of opposite sign to the drop-charges. Since the potential-gradient gives a measure of the charge residing in the lower side of the cloud or below this, it follows that the rain cannot merely bring down the charge of the cloud. On the other hand, if the rain obtains its charge by some process involving the separation of charge, then the negative charge left in the cloud or below, when positive rain falls, might be responsible for the negative potential-gradient often found.

Wilson⁽²³⁾, p. 99) states that the arrival of a cloud without rain usually causes very little change in the vertical potential-gradient, so that there can be little charge resident in the cloud when there is no rain. But it has been found* that, at any rate sometimes, there are considerable charges resident in a cloud which is precipitating ordinary rain, and these usually consist of an upper positive and lower negative charge.

Gschwend⁽¹⁰⁾ found very little correlation between drop-size and drop-charge, so that a theoretical account of the charges on raindrops cannot make use of the differences between drops of different sizes.

It may be pointed out that if the raindrops receive their charges in the cloud, then there must be a space-charge, normally positive, in the region below the cloud owing to the rain itself; this, by itself, would tend to give a potential-gradient of the same sign as the charge on the rain, and so we see that there must remain a larger opposite charge in the cloud. If, on the other hand, the rain receives its charge by processes below the cloud, the charge left in the air will move less rapidly than the raindrops and will give a space-charge of sign opposite to that on the rain, and will give rise to a potential-gradient such as is usually observed; but if there is a large separation of charge in the lower atmosphere, then we should expect an increase in the ionic conductivity, and those methods of measuring the vertical current in rainfall which include the ionic current, i.e. Herath's and Schonland's,

* We are indebted to Dr F. G. W. Whipple, of Kew Observatory, for informing us of the unpublished results obtained by the alti-electrograph in ordinary rain.

should show an ionic current opposite in sign to the rain current; but, in fact, these two methods give the largest positive excess, and there is no evidence for an increase in conductivity in rainy weather. This point might be settled by an exact measurement of the space-charge below clouds during rain.

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DISCUSSION

Dr D. OWEN. It is interesting and surprising to realize that even in a smart shower of rain only a few drops fall in a minute into a receptacle having an aperture of about a square inch, so that the counting of charges on individual drops is not difficult. From the authors' data it appears that the maximum observed charge per drop, of either sign, amounts to about a hundred million electrons, and calculation shows that this is only about 1 per cent of the maximum charge that the dielectric strength of air at atmospheric pressure would permit, while the average raindrop holds only about one-thousandth of the maximum permissible charge. Perhaps the order of these values can be given some definite significance.

Dr F. J. W. WHIPPLE. Observations of the charges on rain and snow must be regarded as fundamental in the development of any theory of atmospheric electricity. In the last few years numerous soundings have been made from Kew with the alti-electrograph, which records the sign of the potential-gradient, and it appears that there are at least two processes at work producing electrification in clouds.

Nearly all rain is melted snow, and in the upper part of a cloud where this snow occurs electricity is probably generated by the collision of the flakes. In the lower part of the cloud the snow flakes have become water drops and these, if they break up, will produce more electrification. Further, it is to be remembered that the charge on a drop will be changed during its descent through the ionized air between cloud and ground. It would be of the greatest interest to obtain information concerning the charges on drops in and just below the clouds. The method described by the authors might be employed in a balloon or at a mountain station, and it is to be hoped that they will endeavour to make further experiments under such conditions.

AUTHORS' reply. We do not at present see any definite significance in the values calculated by Dr Owen.

In reply to Dr Whipple: Our results would suggest that the two processes in the cloud are not sufficient; otherwise, results with snow, when only one process occurs, would be more simple than those with rain, and this is not the case in practice. It would seem that effects beneath the cloud are of importance, and they could be determined by observations in a balloon or at a mountain station, as Dr Whipple suggests. Information could also be obtained by simultaneous measurement of the potential-gradient.

THE MEASUREMENT IN ABSOLUTE UNITS OF THE INTENSITIES OF X-RAY REFLECTIONS FROM CRYSTALLINE POWDERS

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ABSTRACT. The two methods by which the intensities of X-ray reflections from fine powders can be measured absolutely by comparison with reflections from a standard substance are critically examined. The applicability of the mixture method is limited by the necessity for having powders of extremely small *particle size*, of the order of 10^{-5} cm. or less. In the substitution method, the powders are kept separate and the use of such fine powders is not essential; the absolute accuracy of this method is limited by the fact that the absorption coefficients of the two powders have to be known. Experimental results obtained by the two methods for powders of different particle sizes are compared with theoretical results by Schäfer for the effect of particle size on intensities measured by the mixture method. The agreement between the experimental and the theoretical results is sufficiently close to show the usefulness of Schäfer's analysis in determining the magnitude of the error which may occur when the mixture method is used with powders which are not sufficiently fine. A general account is given of a camera designed for use with the substitution method. It allows an alternating interchange of the two powders with a corresponding movement of the photographic film in order to obtain a separation of the photographs corresponding to the two powders.

§ 1. INTRODUCTION

THE most usual and convenient method of obtaining the intensities of X-ray reflections from powders in absolute units is by comparison with reflections from some standard substance, such as NaCl, KCl or aluminium, for which absolute measurements have already been made by a single-crystal method; for reasons which will be discussed in detail elsewhere, we prefer to take finely powdered aluminium as the standard substance. The comparison may be made in two distinct ways. In one method the two powders are intimately mixed and irradiated simultaneously, while in the other the powders are separate and are irradiated alternately; these methods will be called the *mixture method* and the *substitution method* respectively. The actual form of the powder specimen may be either a flat plate or a cylindrical rod, but for intensity-measurements the flat layer has advantages over

the cylindrical rod. In what follows we shall have in mind mainly the case of a flat layer, but usually our remarks will also be applicable to the other case.

The method of mixed powders has been developed and used extensively by Brentano⁽¹⁻⁶⁾ who has indicated in a series of papers the conditions which must be satisfied in order that the method may give accurate results. This method has also been used by Rusterholz⁽¹⁴⁾ and by the present writers^(7,8). There are, unfortunately, difficulties limiting its applicability which led the writers^(9,10,11) and Brentano⁽⁴⁾ to develop an arrangement in which the powders are irradiated separately and alternately and the photographs are separately recorded, although, as we shall show in § 2, the problems which confronted the writers and Brentano were of somewhat different types.

The purpose of the present paper is to review the factors which limit the accuracy of the two methods and to discuss the fields in which they may be used. Experimental results are compared, and it is shown that when differences occur they can be attributed to the unsuitability of the powders for use with the mixture method. Details of a camera for making accurate intensity-measurements by the substitution method are described also.

§ 2. GENERAL CONSIDERATIONS OF THE MIXTURE AND SUBSTITUTION METHODS

In discussing the two methods it will be convenient first to set down the expressions which relate the intensity of the reflected X rays to the crystallographic and geometrical factors of the flat powder block. It can be shown that the total energy I_r reflected from a flat stationary layer of powder of effectively infinite thickness is given by the following expression which was first given by Brentano⁽²⁾ in a somewhat different notation:

$$I_r = C \frac{p N^2 F^2 \rho'}{\mu' \rho} \phi(\theta) A \quad \dots\dots(1),$$

where C is a constant, p is the multiplicity factor for the reflection, N the number of unit cells per unit volume of the crystal, F the amplitude scattered per unit cell, μ' the effective linear absorption coefficient of the powder block, ρ' the effective density of the powder block, ρ the true density of the substance itself, and $\phi(\theta)$ a trigonometrical function involving the glancing angle of reflection θ , which is such that $\phi(\theta) = [1 + \cos^2 2\theta]/\sin \theta \sin 2\theta$. Further, $A = \sin(2\theta - \alpha)/[\sin(2\theta - \alpha) + \sin \alpha]$, and allows for the fact that different reflections leave the powder at different angles, while α is the angle between the incident beam and the powder surface. The constant factor C involves the incident intensity, the wave-length of the radiation and electronic constants.

For a mixture of two very fine powders a common value can be assumed for μ' . If suffixes 1 and 2 then relate to the two components of the mixture it is easy to show that

$$\frac{I_1}{I_2} = \frac{p_1 F_1^2 \phi(\theta_1) A_1 G_1 v_2 M_2}{p_2 F_2^2 \phi(\theta_2) A_2 G_2 v_1 M_1} \quad \dots\dots(2),$$

where G denotes the weight of substance in the mixture, M is the molecular weight of the unit cell and v is the volume of the unit cell.

For the substitution method, we modify equation (1) by introducing the true linear absorption coefficient μ ; since $\mu/\mu' = \rho/\rho'$ we can replace $\rho'/\mu'\rho$ by $1/\mu$. Then, using appropriate suffixes, we obtain for the ratio of the reflected intensities

$$\frac{I_1}{I_2} = \frac{p_1 N_1^2 F_1^2 \phi(\theta_1) A_1 \mu_2 t_1}{p_2 N_2^2 F_2^2 \phi(\theta_2) A_2 \mu_1 t_2} \dots\dots(3),$$

where t_1 and t_2 are the exposure times for the two substances. In the light of these equations certain features of the two methods can now be discussed.

(a) *The mixture method.* The advantages and the limitations of this method have been very fully discussed by Brentano⁽¹⁻⁶⁾ in a series of papers in which he has developed it and only the main features will be set down here as concisely as possible. It is apparent from equation (2) that the intensities of two reflections, one from each substance, can conveniently be controlled by adjusting the factor G_1/G_2 which represents the proportions by weight of the components of the mixture. Since both substances are irradiated simultaneously and under identical conditions, fluctuations of X-ray output are of no consequence. The greatest advantage of the method, however, lies in the fact that the effective linear absorption coefficient can be taken to be the same for both components of the mixture, provided the powders are sufficiently fine, and in consequence the coefficient does not appear in equation (2). The method therefore requires no knowledge of absorption data, which, as will be seen later, is of considerable advantage. The powder particles must, however, be very fine (generally of the order of 10^{-5} cm. in diameter) and it was mainly this limitation which led the writers to develop an alternative method not requiring such very fine powders.

The mixture method is handicapped by the multiplicity of lines recorded from two substances simultaneously; it is often difficult, and perhaps impossible, if the substances have structures other than cubic, to find for comparison suitable pairs of lines which stand clear from neighbouring lines in a manner convenient for accurate photometry. Moreover, discontinuities in the background due to absorption jumps in the general radiation, which Brentano⁽⁴⁾ has discovered, are more troublesome with a mixture of powders than with a single powder.* It was mainly with a view to avoiding superposition of lines and background discontinuities that Brentano developed a method of irradiating the powders separately.

(b) *The substitution method.* Equation (3) shows that in this method a ratio of exposure times replaces the mass-ratio of equation (2) and forms the means by which the reflections from the two powders are controlled to give lines of approximately the same density suitable for photometric comparison. The camera we shall describe later includes a simple mechanical arrangement for alternately raising and lowering a specimen-holder containing two flat parallel layers of powder, so that each powder is irradiated for a known period of time. Coupled with this movement of the powder-holder there is a corresponding movement of the photographic film so that the final result is a strip of film with two exposures, one from each powder,

* Note added in proof: Since this was written, a paper by A. Baxter and J. Brentano has appeared, *Phil. Mag.* **24**, 473 (1937), which discusses these background discontinuities in detail.

side by side for subsequent development under identical conditions. The exposures alternate at fixed intervals adjusted to suit the lines under comparison, so that in a total exposure of an hour or more slow fluctuations of the output of the X-ray tube become unimportant.

A limit to the accuracy of this method arises from the appearance in equation (3) of the absorption coefficients of the two substances. The number of substances and wave-lengths for which accurate absorption data are available is very small, and in general it will be necessary to use an interpolation method to obtain the mass absorption coefficients of the component atoms. By far the most general method for interpolating absorption coefficients is that of Jönsson⁽¹³⁾. Values of μ/ρ for commonly used wave-lengths calculated by Jönsson's method are given by W. L. Bragg in volume 1 of *The Crystalline State*. A comparison of these data with experimental values of μ/ρ , particularly those compiled by S. J. M. Allen and given in *X-rays in Theory and Experiment* by Compton and Allison, shows on the whole a close agreement; the differences are generally not greater than from 1 to 3 per cent. They are occasionally larger, but in many cases where larger differences are found the experimental values are more difficult to obtain, so that the discrepancies may be partly of experimental origin. On the whole it seems probable that the values of μ/ρ obtained by Jönsson's method are reliable to within 3 per cent except for light elements, such that $Z < 10$, and long waves such that $\lambda > 2A$, for which the error may be greater.

The substitution method is particularly suitable for another type of investigation for which the mixture method is ill suited, namely, the direct comparison of two powders of the same substance prepared in different ways. The absorption coefficients will then be the same for the two powders, and when a comparison is made between reflections with the same indices from the two powders, equation (3) reduces to

$$I_1/I_2 = (F_1/F_2)^2 t_1/t_2.$$

The authors^(9,11) have used this method for comparing powders of distorted metals with chemically prepared powders of the same metals, and hence have obtained information as to the nature and magnitude of the distortion. The mixture method was first applied to this problem and gave very misleading results owing to the fact that the particles of filed metal were much too large to satisfy the absorption requirements of the mixture method.

§ 3. THE EFFECT OF PARTICLE-SIZE IN RELATION TO THE MIXTURE METHOD

The effect of particle-size on the X-ray intensities obtained by the mixture method has been considered by Schäfer⁽¹⁵⁾. A simpler and somewhat different treatment has been given by Brentano⁽⁵⁾. Both analyses agree in showing that for the method to give reliable results the particle-size must be so small that there will be negligible absorption in each particle. In practice this means that the

particle-size must be of the order of 10^{-5} cm. or less. It is of interest to compare the deviations to be expected theoretically with those obtained experimentally when the particles are too large. Schäfer's expressions will be briefly stated here and applied to several examples which have arisen in our work and which illustrate the limitations imposed on the use of the mixture method by the absorption in the individual particles.

Consider the reflection of radiation by a particle X , figure 1, in a mixture of two powders, and let AX and XB be the directions of the incident and reflected radiations in the powder. Schäfer shows that the absorption along paths such as $(AX + XB)$ will be the same on the average, whatever kind of particle is at X . If dv is a volume element of the particle at X which is correctly oriented to reflect radiation, then the reflected intensity will be proportional to $e^{-\mu l} dv$, where μ is the linear absorption coefficient and l is the total path of the radiation in the particle. If every element of the particle reflects radiation, the total reflected intensity will be proportional to $\int_V e^{-\mu l} dv$, where the integration is over the volume V of the particle;

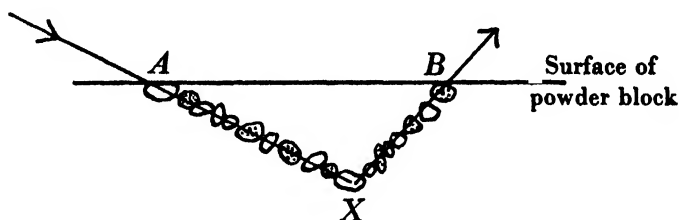


Figure 1

the absorption therefore reduces the reflected intensity by the factor $V^{-1} \int_0^V e^{-\mu l} dv$.

In general, however, only a fraction of each particle will reflect radiation, but if we take into account the fact that a large number of particles will be irradiated, then we can legitimately assume that on the average elements of volume reflecting radiation will be distributed equally in all possible positions in the different particles, so that the effect of absorption will still be to reduce the reflected intensity by the factor $V^{-1} \int_0^V e^{-\mu l} dv$. This will be strictly valid only if the particles are of the same size and orientation, a condition which can never be realized practically, but provided that the particles are of comparable size and devoid of any marked orientation, the expression will give an estimate of the order of magnitude of the effect.

For a mixture, let I_1 and I_2 be the intensities reflected from the two substances. Then the effect of the particle-size of the powders on the ratio I_1/I_2 can be expressed by the ratio K , where

$$K = \frac{\text{observed ratio } I_1/I_2 \text{ for the actual mixture}}{\text{ideal ratio } I_1/I_2 \text{ for particles with negligible absorption}}$$

Alternatively,

$$K = \frac{[I_{\text{observed}}/I_{\text{ideal}}]_1}{[I_{\text{observed}}/I_{\text{ideal}}]_2} = \frac{V_1^{-1} \int_0^{V_1} e^{-\mu_1 v_1} dv_1}{V_2^{-1} \int_0^{V_2} e^{-\mu_2 v_2} dv_2}.$$

In the general case, K cannot be expressed more simply than by this equation, but by assuming particles of simple shape and orientation the integrals can be evaluated and the magnitude of K can be determined. Schäfer has calculated the results for cubic particles of sizes D_1 and D_2 for angles $2\theta = 0^\circ$, 90° and 180° . His results are as follows:

$$\begin{aligned} (a) \quad \begin{array}{c} \uparrow \\ \square \\ \downarrow \end{array} \quad 2\theta = 0^\circ \quad K_0 &= e^{-\mu_1 D_1} / e^{-\mu_2 D_2} \\ (b) \quad \begin{array}{c} \uparrow \\ \square \\ \rightarrow \end{array} \quad 2\theta = 90^\circ \quad K_{90} &= \left\{ \frac{1 - e^{-\mu_1 D_1}}{\mu_1 D_1} \right\}^2 / \left\{ \frac{1 - e^{-\mu_2 D_2}}{\mu_2 D_2} \right\}^2 \\ (c) \quad \begin{array}{c} \uparrow \\ \square \\ \uparrow \end{array} \quad 2\theta = 180^\circ \quad K_{180} &= \left\{ \frac{1 - e^{-2\mu_1 D_1}}{2\mu_1 D_1} \right\} / \left\{ \frac{1 - e^{-2\mu_2 D_2}}{2\mu_2 D_2} \right\}. \end{aligned}$$

§ 4. EXPERIMENTAL RESULTS SHOWING THE EFFECT OF PARTICLE-SIZE ON INTENSITIES MEASURED BY THE MIXTURE METHOD, AND COMPARISON WITH THEORY

Since in this work we are interested primarily in determining the amplitude F scattered per unit cell, it will be convenient to express Schäfer's ratio K in terms of F . Since the reflected intensity is proportional to F^2 , we have

$$K = \frac{(F_1/F_2)^2 \text{ for the actual mixture}}{(F_1/F_2)^2 \text{ for particles with negligible absorption}}.$$

Since the particle-size difficulty is not present with the substitution method, we can find the value of (F_1/F_2) for particles having negligible absorption by using the substitution method, provided we select substances for which the absorption coefficients are known with sufficient accuracy. We may then write for K ,

$$K = \frac{(F_1/F_2)^2 \text{ as obtained by the mixture method}}{(F_1/F_2)^2 \text{ as obtained by the substitution method}}.$$

In table 1 we give three experimental examples in which measurements were made first by the mixture method and secondly by the substitution method. In each case the experimental value of K is worked out and compared with that given by Schäfer's theory. Of course the agreement cannot be expected to be very exact, because each of the powders will consist of particles of various sizes and shapes, but the agreement is sufficiently good to indicate clearly the magnitude of the effect of particle-size on results obtained by the mixture method, and to show that Schäfer's expressions give a fairly reliable estimate of the degree of accuracy to be expected with any given mixture.

Table 1. A comparison of calculated and experimental values of K for various powder mixtures

	Powders	λ (Å.)	μ	Calculated results				Experimental results	
				Particle-size (cm. $\times 10^{-4}$)	K_0	K_{90}	K_{180}	Estimated particle-size (cm. $\times 10^{-4}$)	K
Case I	KCl Cu	1.54	247 471	KCl and Cu of equal size 5 2 0.5	1.12	1.11	1.11	KCl, 5 Cu, 5	For Cu (111), (200), (220) $K = 1.00$
					1.05	1.05	1.04		
					1.01	1.01	1.01		
Case II	KCl Cu	1.54	247 471	KCl, 5 Cu, 20	2.27	2.10	1.97	KCl, 5 Cu, 20	For Cu (111), $K = 1.73$ (a) $K = 1.56$ (b)
Case III	KCl Ni	1.54	247 413	KCl and Ni, 5	1.09	1.08	1.08	KCl and Ni, 5	For Ni (200), $K = 1.00$ $K = 1.29$
	KCl Ni	0.71	28.5 429	KCl and Ni, 5	1.22	1.22	1.21	KCl and Ni, 5	

(a) Chill-cast copper. (b) Hard-drawn copper.

The particle-sizes of the powders were estimated by microscopic examination by viewing the particles against a scale engraved with divisions equal to 10^{-2} cm. In each case it was evident that the bulk of the powder by volume consisted of particles of about the same size. There appeared to be relatively few particles which were markedly larger. There were always present a large number of much smaller particles but these constituted only a small fraction of the total volume of the powder. In estimating the particle-size we have therefore taken an average value for the larger particles, since these form the bulk of the powder and it is on them that the success or failure of the mixture method will depend.

Each of the three cases given in table 1 brings out a point of interest. Case I shows measurements made on chemically prepared powders of KCl and Cu; the agreement between the mixture method and the substitution method is very close, as is seen by the mean value of K for three reflections of Cu measured with respect to KCl being equal to unity. The calculated values of K for equal-sized particles of various values are shown. The observed agreement between the two methods is therefore somewhat better than would be expected from the theory.

In case II, the copper particles were prepared by filing and sieving and are considerably coarser than in the previous example; the same KCl powder was used. The theoretical values of K indicate that large errors would be expected for such a mixture and this is in general agreement with the observed results. The experimental values of K measured for the 111 reflection of copper powder, filed (a) from a chill-cast copper rod, and (b) from a hard-drawn copper wire, are markedly greater than unity, though not so large as the calculated values.

Case III illustrates the fact that a mixture may be suitable for one radiation for which the powders have comparable values of μ but unsuitable for another radiation for which the μ 's differ by a large factor. Thus chemically prepared nickel powder

and KCl give satisfactory results by the mixture method when Cu $K\alpha$ radiation is used but not with Mo $K\alpha$ radiation. The experimental results in this case agree closely with the calculated values.

§ 5. THE EFFECT OF PARTICLE-SIZE AND CRYSTAL-SIZE ON THE MEASUREMENT OF X-RAY INTENSITIES

A clear distinction must be drawn between the effects of particle-size and of crystal-size on the accurate measurements of X-ray intensities. The particles of a powder will not usually be single crystals. With chemically prepared powders, the individual particles consist of clusters of smaller particles which may or may not be single crystals, unless a spacing material is used, as described by Brentano^(5,6), which may be effective in preventing the adherence of the individual crystals to form composite particles. With mechanically produced powders, each individual particle will be an aggregate of much smaller crystals caused by distortion, cleavage and twinning.

The crystal-size of a powder affects X-ray reflections in several ways. In the first place, with extremely small crystals of colloidal dimensions (less than 10^{-6} cm.) there is a broadening of the reflected lines which makes the separation of adjacent lines from each other and of lines from the general background much more uncertain. Secondly, if the crystals are too large, of the order of 10^{-3} cm. or larger, the reflected lines are not continuous but consist of reflections from the individual crystals, and are quite unsuitable for photometry; furthermore, in such a powder too few crystals will be irradiated to satisfy the assumption of a random distribution of the reflecting planes. These two points are important in connexion with the accuracy of the actual measurements. The third point, namely the effect of extinction on the reflected intensities, is important in connexion with the interpretation of the results but has no effect on the accuracy of the measurements.

With powders, primary extinction only is likely to be operative, and this depends on the size of the crystals and on the amplitude reflected per plane in the crystal. Its importance will depend on the nature of the investigation; if it is of an atomic nature, such as the determination of an atomic scattering factor, then extinction should preferably be absent. On the other hand, if the investigation is concerned with a powder in a particular condition, then the intensities must be measured accurately for the powder in this state; the interpretation of the results may or may not be hindered by the presence of extinction.

The particle-size of a powder is important only in connexion with the use of the mixture method for obtaining absolute values, and is unimportant in connexion with the substitution method provided the particles are fine enough to give a specimen with a good surface—a condition which is easily satisfied, and which applies equally to both methods.

The limitation of the particle-size which is necessary in order that the mixture method may be satisfactory, implies also a limitation of the crystal-size to values of the same order as or less than the particle size, and for such small crystals primary

extinction will usually be very small or negligible. This has been expressed by Brentano⁽⁵⁾ in a slightly different way; presupposing that extinction is undesirable, he contends that the ideal aim is to reduce the particle-size so that extinction will be negligible even if the particles consist of single crystals, and there will then be no further difficulty in satisfying the absorption requirements. There is, however, the case of powders having a relatively large particle-size, of the order of 10^{-3} cm. to 10^{-4} cm., which are much too large for the mixture method, and containing much smaller crystallites of the order of 10^{-5} cm.; such powders are produced, for example, when metals and alloys are filed. This case has definitely been considered by Brentano⁽⁵⁾ who has come to the conclusion that "with aggregate particles it is not safe to rely on their subdivision into uniformly small micro-crystallites", and states that he has observed. "not only that in the case of ductile metals like gold, silver and platinum does the tendency exist for microcrystals to unite to larger crystallites, but also that in the case of brittle metals with a high temperature of recrystallization like tungsten some larger crystals are found embodied in the microcrystalline powder when no steps are taken to avoid the formation of large particles; the same thing was found with binary compounds like rock salt". Our own experience has led us to somewhat different conclusions. We have carried out experiments with filed silver and filed rhodium powders and find a large extinction effect; with filed copper and filed nickel powders⁽⁹⁾, however, there is very little extinction, and it affects only the lower orders of reflection appreciably. With filed aluminium⁽¹²⁾ we find no evidence for any extinction. These experiments suggest that with filed metals and alloys of the lighter elements there is little or no extinction.

The situation may be summarized as follows. The mixture method is only applicable when the particle-size is very small, of the order of 10^{-5} cm., and extinction will then usually be absent. The method is therefore limited to powders which can be produced in this extremely finely divided state and to experiments which are not dependent on the use of coarser particles. The substitution method is more generally applicable, since it does not necessitate the restriction of the particle-size to values of the order of 10^{-5} cm. and will give equally accurate values of the reflected intensities whether extinction is present or not. With regard to experiments which require elimination of extinction or its reduction to small values, the evidence so far available suggests that with heavier elements it will generally be desirable to reduce the particle-size to such small values that the mixture method will be applicable, but with lighter elements coarser particles, which may not be suitable for use with the mixture method, may be used. In actual practice there will always be a range of particle-sizes present in a powder, and in border-line cases, where one cannot be certain that the larger particles are not too large for use with the mixture method, it appears to be better to use the substitution method.

§ 6. AN X-RAY CAMERA FOR USE WITH THE
SUBSTITUTION METHOD

Details of the camera are shown by sectional drawings to scale in figures 2*a*, *b* and *c*; subsidiary apparatus for interchanging the powder specimens is shown diagrammatically in figures 2*d* and *e*, which are not drawn to scale.

The camera consists primarily of a metal cylinder with a fine adjustable collimating tube pointing at the axis of the camera to define the incident beam of X-rays. The powder is mounted in a holder of rectangular or circular type so that the surface of the powder lies accurately on the axis of the camera. The reflections emerge through a horizontal slit in the wall of the camera and are recorded on a strip of photographic film wrapped in a holder and attached to the camera with elastic bands. One type of powder-holder, suitable for small quantities of powder, consists of two rectangular parallel cavities which are filled with the powders to be compared. When larger quantities of powder are available, a circular type of holder is used containing two annular cavities having dimensions corresponding to those of the rectangular cavities. This holder is kept in slow rotation in its own plane during the course of an exposure by means of a small motor; this type of holder not only has the advantage of allowing a much larger area of powder to be irradiated, but also makes the results largely independent of any minute imperfections in the powder-surface. The usefulness of the camera is greatly increased by having a number of identical and easily interchangeable specimen holders. A group of eight rectangular holders were machined out of a single bar of mild steel to ensure their having identical dimensions; these are bolted on to a brass metal plate attached to the main shaft of the camera. The circular holders are also interchangeable and are attached to the same brass plate; they are carried by a smoothly finished hollow cylindrical bearing passing through the centre of the brass plate.

The alternating interchange of the powders is effected by raising and lowering the central shaft of the camera by means of a cam *C* operated by the mechanism shown in figures 2*d* and *e*. This consists essentially of a large disc, made of 5-ply wood for the sake of lightness, about 1 ft. in diameter, through the edge of which are bolted two pins (one only is shown in figure 2*d*), at intervals apart suitable for the relative exposures required. The disc is driven by a $\frac{1}{12}$ h.p. synchronous motor through suitable gearing and makes approximately one revolution per minute. As the disc rotates, the pins make contact with four ball-shaped projections on the end of the shaft *S*, so that each time a pin engages one of these projections, the shaft is rotated through 90°; the arrangement is shown in greater detail in figure 2*e*. The other end of the shaft *S* carries the cam *C*, which consists of two similar projections; this is placed under the metal head *H* of the camera. Each quarter turn of the shaft *S* therefore alternately raises and lowers the central shaft of the camera, the movement being just sufficient to move one powder out of and the other powder into the X-ray beam. The relative exposure times are governed by the spacing of the pins. For most purposes it is sufficient to have twenty-four equally spaced holes round the circumference of the disc; if, for example, the pins are placed six

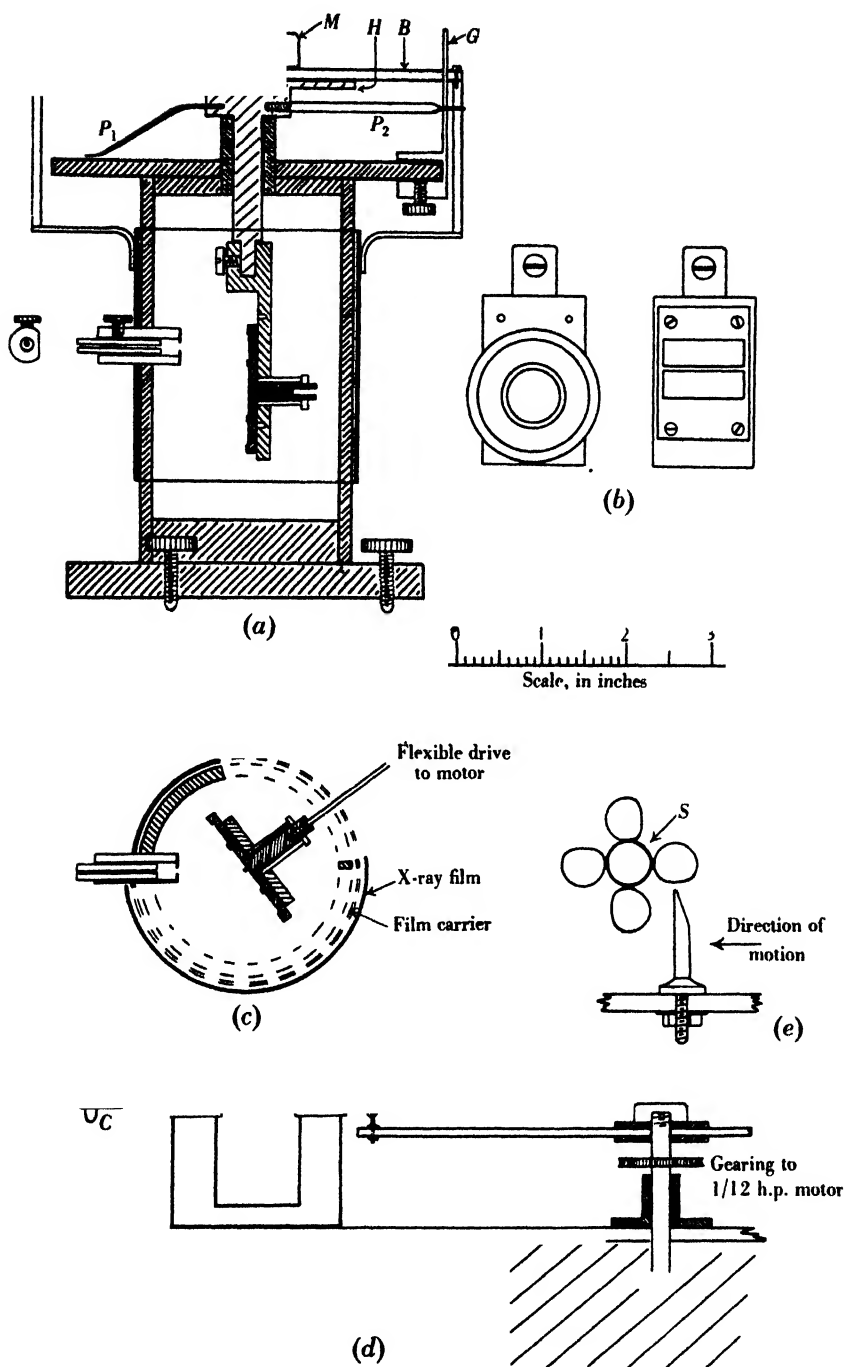


Figure 2. Details of camera and of subsidiary apparatus for interchanging the powder specimens. Figures (a), (b) and (c) are drawn to scale; figures (d) and (e) are diagrammatic.

holes apart, the powder holder will be in one position, raised or lowered, while six holes pass the shaft *S* and in the other position while eighteen holes pass, so that the ratio of the exposure times will be 1 : 3. In actual use we do not rely on this arrangement of holes to give us the correct ratio, but measure it directly with a clock at intervals during the exposure; the measured ratio agrees to within 1 or 2 per cent with the calculated ratio.

To avoid superposition of the reflections from the two powders, which would happen with a stationary film, the film is mounted on a cylinder surrounding the main body of the camera which is carried by a bar *B* passing across the top of the camera and firmly clamped to the central shaft by a large milled clamping-nut *M*. By this means, the movement of the film carrier is coupled with that of the powder-holder; the film, when developed, shows side by side two photographs from the two powders. A typical photograph—but over-exposed for the sake of good reproduction—is shown in figure 3; it shows a comparison of the 220 and 311 reflections of aluminium and the 420 and 422 reflections of potassium chloride.

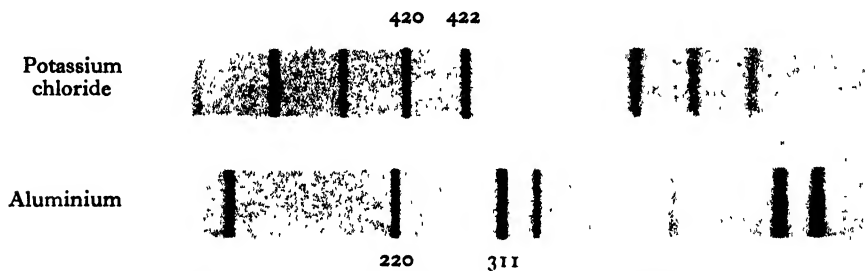


Figure 3. Typical photograph, showing comparison of potassium chloride and aluminium reflections.

Details of the top of the camera will now be described. When the milled nut *M* is unscrewed, the horizontal bar *B* to which the film carrier is attached and the central shaft carrying the powder holder, can be turned freely and independently. The setting of the powder-surface with respect to the incident X-ray beam is effected by means of the fine pointer *P*₁ moving over a graduated scale on the top surface of the camera. The setting is finally secured by means of a second pointer *P*₂ which slides in the vertical guide *G* clamped to the rim of the camera; this guide further ensures absence of any rotation when the powder-holder is raised or lowered. The up-and-down movement of the film carrier is obtained by its attachment to the bar *B* and any rotational movement is prevented by screwing down the milled nut *M* firmly and also, incidentally, by the slit rendered necessary by the collimator.

The X-ray reflections emerge from the camera through a slit $\frac{1}{4}$ in. wide in the main body of the camera which extends from a scattering angle of 0° almost to 180°; the extent of this slit is indicated in figure 2*c*. Owing to the vertical movement of the film carrier, it is necessary for the corresponding slit in the film carrier to be slightly more than $\frac{1}{2}$ in. wide; the difference between the two slit-widths is in fact equal to the vertical motion of the film which must also be equal to the distance

between the centres of the two rectangular powder cavities. The circular powder holder is kept in rotation by means of a small motor connected by a very light flexible drive, which passes through a second slit in the wall of the camera as shown in figure 2c; this slit is made about $\frac{3}{4}$ in. wide in the camera and the corresponding slit in the film carrier is about 1 in. wide. The angular range of these slits is shown in figure 2c.

The details of the collimating system are shown on the left of figure 2a. It consists of a brass tube, $\frac{3}{8}$ in. in diameter, with a central hole of diameter $\frac{1}{8}$ in. into which suitable collimating tubes can be inserted. The side of the brass tube is cut away so that reflections can be recorded as nearly as possible up to 180° . A small screw holds the inner collimating tube firmly. We have found it most satisfactory to use fine collimating tubes made out of a lead-bismuth-antimony alloy (70 per cent lead, 15 per cent bismuth and 15 per cent antimony). As regards its absorption properties, this alloy is as satisfactory as pure lead and being much harder it has the advantage that it can be turned in the lathe and given a good finish. The edges of the brass cylinder are covered with lead foil, as also is the interior of the camera. A range of collimators has been constructed having diameters of 1 mm., $\frac{1}{2}$ mm. and $\frac{3}{8}$ mm., and lengths 2 cm., 1.5 cm. and 1 cm.

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THE KINETIC THEORY OF FLUIDS

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ABSTRACT: The kinetic theory is applied to the properties of real fluids by including the effect of molecular attraction. The observed properties of individual substances are calculated directly by pure dynamics from the attraction of their ultimate particles, thermal agitation and volume only, without the introduction of any arbitrary factors. The mutual attraction of the molecules of real substances increases their mean square velocity. Maxwell's law is modified by the introduction of a parameter λ which multiplies the most probable speed of the molecules, λ being the ratio of the most probable speed in a real fluid to that in an ideal gas. Other necessary consequences of molecular attraction are that all real gases and liquids are associated; there is at every interface an adsorbed layer which modifies the average effect of the transfer of momentum in collision, and there is a change of energy, due to variation of λ , in passing from one medium into another. These effects have been calculated. In order to apply the results, a law of force must be adopted. Edser's inverse-eighth-power law is found to hold. The method is applicable to all the physical properties of fluids and is applied, by way of example, to the equation of state of a gas and the vapour pressure and viscosity of a liquid with satisfactory results. The new theory explains the observed decrease of viscosity of liquids with temperature, without which no theory can be accepted.

§ 1. INTRODUCTION

THE present paper, which extends the kinetic theory to real fluids, is developed on classical lines without any empirical assumptions, and it is shown that a very close approximation to the behaviour of real liquids may be obtained by a straightforward dynamical treatment, without recourse to quantum considerations such as those discussed by Lennard-Jones⁽¹⁾. The method developed does not depend on any particular law of force, but in order to test the formulae obtained, by comparison with experimental results some law of force is necessary. The law adopted is the inverse eighth power, deduced by Edser in a valuable paper contributed to the British Association Reports on Colloid Chemistry⁽²⁾. The line of approach of the present paper differs from that adopted by Andrade⁽³⁾, who considers the subject from the point of view of the solid state.

Maxwell's law of the distribution of molecular velocities is assumed. This is applied to molecules possessing attraction by the introduction of a parameter λ which governs the most probable speed of the molecules in a particular medium, λ being different for different media. This leads to a new theory of physics in which molecular attraction is as essential as is gravitation to astronomy, and the observed values of the properties of gases and liquids can be calculated directly from their coefficients of attraction. It is shown that all gases and liquids are associated in greater or less degrees.

The equation of state of a fluid,

$$A(p + K)(v - b) = \lambda^3 RT,$$

is similar to that of van der Waals, except in including two essential new factors, A , the association, and λ . These explain the deviations of real gases from the old van der Waals equation and imply that low-temperature measurements are subject to serious error on account of the neglect of these terms, which become very important as the liquid state is approached.

The form of the factor representing transfer of momentum in collision is determined for liquids of changing density.

The cohesion, K , and the surface tension, S , of liquids having been evaluated as functions of the molecular attraction of their ultimate particles, a quantitative account of the phenomena of vaporization is given and the actual vapour pressures, boiling points, and viscosities of liquids are calculated directly from molecular attraction, volume and motion only, without the introduction of any arbitrary factors.

The formulae so deduced are applied to the calculation of the properties of elements and compounds, organic and inorganic, polar and non-polar, and ranging from the lightest gas to the heaviest liquid. The same methods are applicable to the whole field of molecular physics.

§ 2. MOLECULAR ATTRACTION

Molecular attraction is unquestionably the cause of the liquid and solid states. Lack of attention to this fact has been the cause of the failure of earlier attempts to establish a complete kinetic theory of liquids and gases. Such a theory must include a definite law of force. The law adopted here is Edser's inverse eighth power⁽²⁾.

However, although it has been sufficient to adopt the simple law of force

$$f = \mu r^{-8} \quad \dots\dots(2.1)$$

in the present paper, it is necessary to recognize that molecules are electrically neutral, and that, while in some orientations they attract one another, in others they repel. The apparent resultant attraction may be due to the nearer approach, or longer duration, of the attractive encounters. The importance of molecular attraction is evident from the present paper. Attention should now be directed to deducing a complete law of force which will take into account the orientation of the colliding molecules and the differences in the nearest distances of approach in attractive and repulsive encounters. It should then be possible to extend the present theory to the consideration of the transition from liquid to solid, which depends on the fact that the attraction of solid particles, oriented in the most favourable position, is greater than that of liquid particles, which are able to assume any orientation. The physical properties of solids can then be calculated, and it may be possible eventually to include the treatment of chemical combination. In the meantime we must bear clearly in mind that the simple law of force mentioned above may not apply to the solid state.

§ 3. MAXWELL'S LAW IN THE CASE OF ATTRACTING MOLECULES

As Kleeman showed^(4, 5), molecular attraction must make the average velocity of the molecules in a real substance greater than that in an ideal gas at the same temperature. In a real fluid a large number of moving points must exist, at which the instantaneous resultant of the molecular forces is zero. The velocities of molecules passing through these points are the same as in an ideal gas. But at other points the molecules are under the influence of the forces exerted by the surrounding molecules where, by the definition of force, their velocities cannot be the same as they would be if no forces were acting. It follows, therefore, that the average velocity of a molecule of a real substance is greater, and in the case of liquids and solids very much greater, than in an ideal gas.

In this paper it is assumed that the distribution of molecular velocities in a real fluid follows Maxwell's law, but with a different most probable speed α , which is greater than the most probable speed P in an ideal gas, as expressed by the equation

$$\alpha = \lambda P \quad \dots\dots(3.1),$$

where λ is a parameter of fundamental importance, expressing the ratio of the most probable speed of the molecules in a real fluid to that in an ideal gas at the same temperature. It will be seen that Maxwell's formulae in their original form are applicable to real fluids, provided that there is no change of phase. But in transition from one phase to another α is not constant.

Thus, the number of molecules of a real fluid which have the X component of their velocities between u and $u + du$ at any instant is

$$n_u = \frac{n}{\sqrt{\pi} \cdot \lambda P} e^{-u^2/\lambda^2 P^2} du, \quad \dots\dots(3.2)$$

and so on. Similarly the average-kinetic-energy velocity C_r , whose square multiplied by half the mass of a molecule represents the average kinetic energy of a fluid, is given by

$$C_r^2 = \frac{3}{2} \alpha^2 = \frac{3}{2} \lambda^2 P^2 \quad \dots\dots(3.3).$$

§ 4. TEMPERATURE

The realization of the fact that the most probable speeds of the molecules of real fluids at the same temperature are different leads to a new definition of temperature. Temperature Θ is now defined as the mean kinetic energy of a particle of an ideal gas in equilibrium with the substance under observation. Or

$$\Theta \equiv \frac{1}{2} m C^2 \quad \dots\dots(4.1)$$

$$= \frac{1}{2} m C_r^2 / \lambda^2 \quad \dots\dots(4.2).$$

The dimensions of temperature are therefore given by

$$[\Theta] = [ML^2 T^{-2}] \quad \dots\dots(4.3).$$

This definition gives a definite physical meaning to temperature and a clear

insight into thermal changes, which can now be treated directly by means of the kinetic theory without the introduction of any thermodynamical methods.*

The following formulae follow immediately:

$$C^2 = \frac{2\Theta}{m}, \quad P^2 = \frac{4}{3} \frac{\Theta}{m}, \quad \alpha^2 = \frac{4}{3} \frac{\lambda^2 \Theta}{m} \dots\dots(4.4, 4.5, 4.6).$$

§ 5. MOLECULAR ASSOCIATION

Before passing to the deduction of the equation of state of a fluid it is necessary to consider one of the most important consequences of molecular attraction, i.e. association. There is considerable evidence that vapours do not condense to liquids, nor liquids assume the solid state, without passing through an intermediate stage in which the vapour or liquid particles are aggregated. It is, indeed, inconceivable that a gas could suddenly change into a liquid without assuming an intermediate condition in which its particles were associated. But association is not confined to the phenomenon of change of state. Having admitted the fact of molecular attraction we are forced to recognize that no real fluid, at any temperature, is unassociated. From the law of distribution of molecular velocities which has been adopted it follows that, at any temperature, always some pairs of molecules in collision will possess relative velocities that are less than the critical velocity required to overcome their mutual attraction. These pairs will become associated and remain in that condition until the association is broken by interaction with other molecules in the molecular chaos. In the noble gases, which have a very small cohesion, the critical velocity is also very small, and the number of associated molecules is almost negligible at ordinary temperatures and pressures. But, even these substances are considerably associated at low temperatures or high pressures. For all other gases molecular association is an essential fact under most conditions. An approximate formula for the association of a gas has been obtained by the methods of this paper. This formula has been used to calculate the values of association of the gases and vapours in table 1. A more accurate expression is now being deduced and will be communicated in a subsequent paper.

§ 6. THE EQUATION OF STATE OF A FLUID

Whatever be the law of molecular attraction, across any plane in the interior of a real homogeneous fluid there is a pressure K which is due to the mutual attraction of the particles of the fluid. This is termed the *cohesion* of the fluid. This pressure, together with the pressure p upon the walls of the containing vessel and the free surface of the fluid, is balanced by the expansion pressure p_e of the fluid particles moving across the plane. Or

$$p_e = p + K \dots\dots(6.1).$$

* The quantity of heat U in a g.-mol. of an ideal gas is given by

$$U = \frac{1}{2} NmC^2 = N\Theta.$$

In the case of a real fluid this becomes

$$U = N(1 + \beta)\lambda^2\Theta \dots\dots(4.5),$$

where β refers to the internal energy of the molecules.

The number of molecules per second, in unit volume of the liquid, having the components of their velocities normal to the plane between u and $u + du$ is

$$\frac{n}{\sqrt{\pi} \cdot \alpha} e^{-u^2/\alpha^2} du.$$

The number of these that strike unit area of the plane per second will be this number multiplied by the speed u , i.e.

$$\frac{n}{\sqrt{\pi} \cdot \alpha} e^{-u^2/\alpha^2} u du.$$

The partial pressure across the plane exerted by these molecules is their number multiplied by their change of momentum $2mu$. This pressure is, therefore,

$$\frac{2mu}{\sqrt{\pi} \cdot \alpha} e^{-u^2/\alpha^2} u^2 du.$$

The total pressure p_e is obtained by integration from $u=0$ to $u=\infty$. This gives

$$p_e = \frac{1}{2} mn\alpha^2 \quad \dots\dots(6.2).$$

Thus from equation (4.6) we obtain

$$(p + K) = \frac{2}{3} n\lambda^2\Theta \quad \dots\dots(6.3).$$

If v is the volume of 1 g.mol., we have

$$n = N/(v - b) \quad \dots\dots(6.4),$$

where

$$N = 6.06 \times 10^{23} \quad \dots\dots(6.5),$$

and

$$b = \frac{2}{3} \pi \sigma^3 N \quad \dots\dots(6.6)$$

$$= 1.300 \times 10^{24} \quad \dots\dots(6.7),$$

σ being the average of the nearest distances of approach of the centres of two molecules in a great many collisions.

The formula (6.4) applies to all problems involving the transfer of momentum during collision of molecules in a homogeneous fluid. It may be written

$$n = \frac{N}{v} \cdot \frac{v}{v - b} \quad \dots\dots(6.8),$$

where $v/(v - b)$ will be termed the *collision factor*. In the sequel the form of this factor for a medium of varying density is obtained.

On the introduction of the association factor A , equation (6.3) becomes

$$(p + K) = \frac{2}{3} \frac{N}{A(v - b)} \cdot \lambda^2 \Theta \quad \dots\dots(6.9).$$

Transposing, we have

$$A(p + K)(v - b) = \lambda^2 P \Theta,$$

where P is a constant defined by the equation

$$P \equiv \frac{2}{3} N \quad \dots\dots(6.10).$$

Changing from c.g.s. to centigrade units we obtain

$$A(p + K)(v - b) = \lambda^2 RT \quad \dots\dots(6.11).$$

This is the equation of state of a real fluid. If it were possible to neglect the factors A and λ^3 , the equation would be the same as that of van der Waals. It is now clear that his equation, although only approximate, was based on sound principles but could not represent the behaviour of gases and liquids accurately, because it neglected two important effects of molecular attraction.

The new equation represents satisfactorily the pressure, volume and temperature relations of pure gases and liquids. Nevertheless, we are not entitled to assume that it can be applied to the change from vapour to liquid and vice versa, because the energy transfers have not been considered. These changes will be investigated in the next section.

By writing $A = 1$, $K = 0$, $b = 0$, and $\lambda = 1$, the well-known Boyle's law is obtained

$$pv = RT \quad \dots\dots(6.12).$$

Since these last four equations are untrue, the method shows that Boyle's law does not apply to real fluids, and indicates very clearly the errors involved in thermodynamic analysis. By making the assumption that hydrogen obeys Boyle's law, we find

$$\Theta = 5.62 \times 10^{-14} \quad \dots\dots(6.13)$$

at 273°K. , since

$$P = 4.04 \times 10^{23} \quad \dots\dots(6.14).$$

The absolute zero of temperature on the c.g.s. scale is simply that at which molecules have no velocity of translation. Therefore $5.6 \times 10^{-14^\circ} \text{E.}$ are equivalent to 273°K. , or

$$1^\circ \text{E.} = 4.86 \times 10^{15^\circ} \text{C.} \quad \dots\dots(6.15),$$

$$1^\circ \text{C.} = 2.06 \times 10^{-16^\circ} \text{E.} \quad \dots\dots(6.16).$$

This latter expression means that a centigrade degree is equivalent to $2.06 \times 10^{-16} \text{erg.}$ We have also

$$\frac{\Theta}{T} = \frac{R}{P} = 2.06 \times 10^{-16} \quad \dots\dots(6.17).$$

More exact figures derived from the equation of state will be communicated in a subsequent paper.

§ 7. VAPORIZATION AND CONDENSATION

Consider a pure liquid in equilibrium with its vapour only and maintained at a constant temperature Θ in a thermostat under ordinary laboratory conditions, so that any heat abstracted from the liquid by the escaping vapour will be supplied immediately by the enclosure, while any heat gained by the vapour will be given up to the surroundings.

At the common surface of the liquid and vapour there is a rapid gradation in density from that of the liquid to that of the vapour. In the first place, it will be assumed that in passing from the liquid to vapour and vice versa the density changes abruptly. The effect of the gradual change, which is very important, will be discussed in the sequel. The vapour of the liquid must be formed by particles that

approach the surface of the liquid with the components of their velocities normal to the surface equal to or greater than a critical speed s which is sufficient to carry them through the surface of the liquid against the attraction of the liquid particles. The escaping particles are helped in their passage by the attraction of the vapour particles. But if the vapour is not dense this effect is inappreciable. The number of particles of the liquid striking unit area of the surface per second which have the components of their velocity normal to the surface equal to or greater than s is

$$n_l' = \frac{n_l \alpha_l}{2\sqrt{\pi}} e^{-s^2/\alpha_l^2} \quad \dots\dots(7.1),$$

where the subscript l refers to the liquid phase. Similarly, the total number of particles from the vapour that strike the same area of surface per second is

$$n_g' = \frac{n_g \alpha_g}{2\sqrt{\pi}} \quad \dots\dots(7.2),$$

the subscript g being used to indicate the vapour phase. The greater attraction of the liquid ensures that all these particles return to the liquid. In equilibrium, the number of particles escaping from the liquid must be equal to the number of those returning, or

$$\frac{n_l \alpha_l}{2\sqrt{\pi}} e^{-s^2/\alpha_l^2} = \frac{n_g \alpha_g}{2\sqrt{\pi}} \quad \dots\dots(7.3).$$

If, now, we consider the kinetic energy carried by the molecules in their passage to and from the liquid, we find that the total energy of all the molecules passing into the vapour per second through unit area of surface is

$$n_l' \left(\frac{1}{2} m s^2 + \frac{1}{2} m \lambda_l^2 P^2 \right) \quad \dots\dots(7.4).$$

Of these molecules, one having its vertical component exactly equal to s would arrive at the surface with no kinetic energy. The energy $\frac{1}{2} m s^2$ represents the work done in escaping from the liquid. The remainder, i.e. $\frac{1}{2} m \lambda_l^2 P^2$, is the average kinetic energy carried into the vapour by the capable molecules. Similarly, the molecules passing down from the vapour into the liquid bring with them the following kinetic energy per square centimetre per second :

$$\frac{1}{2} n_g' m \lambda_g^2 P^2.$$

Or, since λ_g is practically unity,

$$\frac{1}{2} n_g' m P^2 \quad \dots\dots(7.5).$$

In equilibrium the transfer of energy in both directions must be the same. Consequently

$$\frac{1}{2} m \lambda_l^2 P^2 = \frac{1}{2} m P^2 \quad \dots\dots(7.6),$$

which gives

$$\lambda^2 = 1.$$

This simple arithmetic has been accepted as final evidence that the molecular forces do not affect the motions of molecules, which means that Newton's laws of motion apply in some cases and not in others. If this deduction were true, we might well accept the dictum that it is impossible to understand the physical construction of the universe. However, further inspection shows that the analysis

has not been made to conform to the physical facts. We have not allowed for the variation of λ through the liquid-vapour interface. Particles entering the liquid from the vapour acquire kinetic energy additional to their temperature energy in the vapour state, on account of the attraction of the liquid particles. This energy is distributed through the liquid and is represented by the factor λ . Thus particles in the liquid possess, in respect of their λ , a certain kinetic energy in excess of the temperature energy corresponding to that of a perfect gas, and this energy is capable of doing work when the particles escape from the attractive forces. If we write W_λ as the average work that a particle can do in virtue of its λ in escaping from the liquid into the vapour, the total work W_s necessary to overcome the surface forces may be diminished by this amount in calculating s . Or,

$$W_s = W_s - W_\lambda \quad \text{.....(7.7).}$$

Referring again to equation (7.4) we see that, on an average, a particle passing through the surface from the liquid to the vapour contributes the energy it possesses on account of its λ towards overcoming the surface forces, and arrives in the vapour with the average kinetic energy $\frac{1}{2}mP^2$, and not $\frac{1}{2}m\lambda^2P^2$. The difference between these two quantities represents W_λ . Or,

$$W_\lambda = \frac{1}{2}mP^2(\lambda^2 - 1) \quad \text{.....(7.8).}$$

We see therefore that equation (7.6) is untrue and

$$\lambda^2 \neq 1.$$

We may now return to equation (7.3) from which, by substituting the values of n and α from (6.8) and (4.6), and putting

$$s^2 = 2W_s/m \quad \text{.....(7.9),}$$

we obtain

$$\frac{A_l(v_l - b)}{A_g(v_g - b)} \frac{\lambda_g}{\lambda_l} = e^{-W_s/\frac{1}{2}\lambda_l^2\Theta} \quad \text{.....(7.10).}$$

Now the behaviour of the vapour phase is represented by equation (6.10). Elimination of $A_g(v_g - b)$ between these two equations gives

$$p + K_g = \frac{\lambda_g \lambda_l P \Theta}{A_l(v_l - b)} e^{-W_s/\frac{1}{2}\lambda_l^2\Theta} \quad \text{.....(7.11),}$$

or

$$p = \frac{\lambda_l P \Theta}{A_l(v_l - b)} e^{-W_s/\frac{1}{2}\lambda_l^2\Theta} \quad \text{.....(7.12),}$$

since K_g and λ_g are comparatively very small.

It will be noticed that the first term in the expansion of the expression in the right-hand side of the last equation but one gives an equation similar to the equation of state, except that λ^2 is replaced by $\lambda_g \lambda_l$. It is clear that while the latter equation is true for a gas or vapour, it does not hold for a liquid which is giving off vapour.

In the vaporization expression it has been assumed that, for every liquid particle that approaches the surface in the state of aggregation corresponding to the degree of association in the liquid, a simple unassociated particle is transmitted to the vapour. In the present state of our knowledge it is impossible to determine

whether these conditions hold exactly, or to allow for any energy-change involved in dissociation. There is, however, a further correction which can be introduced. As we have seen, the particles of the vapour must be associated. The number of particles which return to the liquid is

$$\frac{n_g \alpha_g}{2\sqrt{\pi}}.$$

The total mass of these particles is $A_g n_g \times m$, and their average most probable speed

$$\alpha_g = \frac{P}{\sqrt{A_g}} \quad \dots\dots(7.13).$$

As, in equilibrium, the total masses of the escaping and returning particles must be the same, we have, omitting m from both sides,

$$\frac{n_l \lambda P}{2\sqrt{\pi}} e^{-\epsilon^2/\alpha_l^2} = \frac{A_g n_g \cdot P/A_g^{\frac{1}{2}}}{2\sqrt{\pi}} \quad \dots\dots(7.14)$$

instead of equation (7.3). Consequently the vaporization equation (7.12) becomes

$$p = \frac{A_g^{\frac{1}{2}} \lambda_l P \Theta}{A_l (v_l - b)} e^{-W_s/\frac{1}{2}\lambda_l^2 \Theta} \quad \dots\dots(7.15).$$

Up to this point the analysis is independent of the law of force which governs molecular attraction. In order to apply the formulae to the behaviour of liquids it is necessary to deduce, from a definite law of force, the value of the cohesion of liquids and of the work done by escaping particles.

§ 8. THE ESCAPE OF A PARTICLE FROM A LIQUID

To find the attraction of the liquid on an escaping particle, let P_1 be the centre of a particle at a distance x below the surface AB of the liquid, where $x > \sigma$. The attraction of the particles of the liquid on P_1 may be taken as exerted by a continuous mass of liquid above AB . Particles in this supposed mass of liquid, whose centres would be between two planes parallel to AB , at distances ξ and $\xi + d\xi$ above AB , would exert on P_1 a resultant attraction equal to

$$\begin{aligned} & \frac{2\pi n \mu d\xi}{(x+\xi)^6} \int_0^{\frac{1}{2}\pi} \cos^2 \theta \sin \theta d\theta \\ &= \frac{2\pi n \mu d\xi}{7(x+\xi)^6} \quad \dots\dots(8.1). \end{aligned}$$

The total attraction on P_1 by all the particles whose centres would be above AB would be equal to

$$\frac{2\pi \mu n}{7} \int_0^\infty \frac{d\xi}{(x+\xi)^6},$$

which

$$= \frac{2\pi \mu n}{35x^5} \quad \dots\dots(8.2).$$

When the distance below the surface of AB of the escaping particle at P_2 becomes less than σ , that part above AB of a sphere with radius σ described around

the particle would contain no centre of an attracting particle. The attracting molecules above AB may now be considered to have their centres within the portions above AB of two spheres with radii r and $r + dr$ described around the molecule at P_2 . The resultant attraction on P_2 by molecules whose centres would lie between the surfaces of these spheres would be

$$\begin{aligned} & \frac{2\pi\mu n dr}{r^6} \int_0^{\cos^{-1}(a/r)} \cos \theta \sin \theta d\theta \\ &= \frac{\pi\mu n dr}{r^6} \left(1 - \frac{x^2}{r^2}\right) \end{aligned} \quad \dots\dots(8.3),$$

and the total attraction on P_2 by all the molecules whose centres would be above an imaginary sphere with radius σ would be

$$\begin{aligned} & \pi\mu n \int_{\sigma}^{\infty} \left(\frac{1}{r^6} - \frac{x^2}{r^8}\right) dx, \\ &= \pi\mu n \left(\frac{1}{5\sigma^5} - \frac{x^2}{7\sigma^7}\right) \end{aligned} \quad \dots\dots(8.4).$$

which

The work done by the molecule in escaping to the surface of the liquid is, therefore,

$$\frac{2\pi\mu n}{35} \int_{-\infty}^{-\sigma} \frac{dx}{x^5} + \frac{\pi\mu n}{\sigma^5} \int_{-\sigma}^0 \left(\frac{1}{5} - \frac{x^2}{7\sigma^2}\right) dx,$$

which

$$= \frac{\pi\mu n}{6\sigma^4} \quad \dots\dots(8.5).$$

An equal amount of work must be done by the molecule in escaping completely from the surface to infinity, so that the total work done by a particle of liquid in passing into the vapour is

$$W_v = \frac{\pi\mu n_l}{3\sigma^4} \quad \dots\dots(8.6).$$

It should be noticed that the attraction of the vapour particles on the escaping particles has been neglected. It is easy to introduce the necessary correction, if desired, but at ordinary pressures this is not necessary. We can now determine the cohesion of a fluid.

§ 9. THE COHESION OF A FLUID

The cohesion K is defined as the attraction across an imaginary plane in the fluid exerted by all particles on one side of the plane for all the particles on the other side of the plane. Consider a plane AB drawn in the liquid. As in the previous section, the attraction exerted on any particle at a distance x below the plane, where $x > \sigma$, by all the particles on the other side of the plane is

$$2\pi\mu n/35x^5.$$

Therefore the attraction per unit area of AB exerted by all the particles above AB on all the particles below AB , whose centres are at distances greater than σ , is

$$\frac{2\pi\mu n^2}{35} \int_{-\sigma}^{-\infty} \frac{dx}{x^5} = \frac{2\pi\mu n^2}{140\sigma^4} \quad \dots\dots(9.1).$$

Similarly, for particles at distances below AB that are less than σ , the total attraction per unit area is

$$\frac{\pi\mu n^2}{\sigma^5} \int_0^{-\sigma} \left(\frac{1}{5} - \frac{x^2}{7\sigma^2} \right) dx = \frac{16\pi\mu n^2}{105\sigma^4} \quad \text{.....(9.2).}$$

The total attraction across the plane, or the cohesion, is equal to the sum of the expressions (9.1) and (9.2), which gives

$$K = \frac{\pi\mu n^2}{6\sigma^4} = \frac{\pi\mu N^2}{6\sigma^4 v^2} \quad \text{.....(9.3).}$$

Similarly for a mixture or an associated fluid

$$K_{12} = \frac{\pi}{\sigma^4} \left\{ \frac{\mu_1^{\frac{1}{2}} n_1}{\sigma_1^2} + \frac{\mu_2^{\frac{1}{2}} n_2}{\sigma_2^2} \right\}^2 \quad \text{.....(9.4).}$$

§ 10. THE SURFACE TENSION OF A LIQUID

The surface tension may be determined very simply by Gauss's method: the surface tension S is equal to half the work W done per unit area of a surface AB described within a liquid in separating the liquid above AB from that below it. We have seen that the attraction of all the liquid molecules below AB on a molecule at a distance x above AB , where $x > \sigma$, is

$$2\pi\mu n/35x^5 \quad \text{.....(10.1).}$$

The work done in removing this molecule to infinity is obtained by integrating this expression multiplied by dx from x to ∞ , which gives

$$\pi\mu n/70x^4 \quad \text{.....(10.2).}$$

Describe two planes parallel to AB at distances x and $x+dx$ above AB . Unit area of the liquid between these planes will contain ndx molecules. The work of removing these to infinity will be

$$\frac{\pi\mu n^2}{70x^4} dx \quad \text{.....(10.3).}$$

Therefore the work W_1 of removing to infinity the whole of the liquid molecules originally at a distance σ or more above AB is given by

$$\begin{aligned} W_1 &= \frac{\pi\mu n^2}{70} \int_{\sigma}^{\infty} \frac{dx}{x^4} \\ &= \frac{\pi\mu n^2}{210\sigma^3} \quad \text{.....(10.4).} \end{aligned}$$

When, however, the distance x of a molecule above $AB < \sigma$, the attraction on this molecule of all molecules below AB is

$$\frac{\pi\mu n}{\sigma^5} \left(\frac{1}{5} - \frac{x^2}{7\sigma^2} \right) \quad \text{.....(10.5).}$$

To remove this molecule from x to a distance σ requires an expenditure of energy equal to

$$\frac{\pi\mu n}{\sigma^5} \int_x^\sigma \left(\frac{1}{5} - \frac{x^2}{7\sigma^2} \right) dx,$$

which

$$= \frac{\pi\mu n}{\sigma^5} \left(\frac{\sigma - x}{5} - \frac{\sigma^3 - x^3}{21\sigma^2} \right) \quad \dots\dots(10.6).$$

The work per unit area of AB necessary to remove to a distance σ all the molecules originally at distances between 0 and σ above AB is, therefore,

$$\frac{\pi\mu n^2}{\sigma^5} \int_0^\sigma \left(\frac{\sigma - x}{5} - \frac{\sigma^3 - x^3}{21\sigma^2} \right) dx,$$

or

$$W_2 = \frac{9\pi\mu n^2}{140\sigma^3} \quad \dots\dots(10.7).$$

Now the layer of liquid above AB comprises $n\sigma$ molecules per unit area of AB . The above is the work of removing these molecules to a distance σ above AB . The work of removing a single molecule from a distance σ to infinity is found by substituting σ for x in expression (10.2), which gives

$$\pi\mu n/70\sigma^4 \quad \dots\dots(10.8).$$

Therefore the work W_3 of removing $n\sigma$ molecules to infinity is given by

$$W_3 = \pi\mu n^2/70\sigma^3 \quad \dots\dots(10.9).$$

Consequently the total work W of removing to infinity all the mass of liquid above AB is given by

$$W = W_1 + W_2 + W_3.$$

We have now created two surfaces of separation, one at AB and one at infinity. Consequently the energy S of one free surface is given by

$$S = \frac{1}{2}W,$$

or

$$S = \pi\mu n^2/24\sigma^3 \quad \dots\dots(10.10).$$

Similarly for a mixture

$$S = \frac{\pi}{24} \left\{ \frac{\mu_1^{\frac{1}{2}} n_1}{\sigma_1^{\frac{3}{2}}} + \frac{\mu_2^{\frac{1}{2}} n_2}{\sigma_2^{\frac{3}{2}}} \right\}^2 \quad \dots\dots(10.11).$$

§ 11. THE EFFECTS OF VARYING DENSITY

In the previous discussion it has been assumed throughout that the density of the liquid changes abruptly at the surface to that of the vapour. Although the region through which this change takes place is very narrow, its thickness is considerable compared with the effective diameter of a molecule. There can be no doubt that within this region the change of density is not abrupt but continuous. It is now necessary to enquire how this gradual transition affects the calculations we have been making. So far it has not been possible to evaluate the change of density through the surface of a liquid. But Mr E. Lancaster-Jones has shown in the following lemma that, apart from the effect of the transfer of momentum during

collision, which will be considered hereafter, the density-change does not affect the work done by a particle in escaping through the surface, provided the function expressing the variation of n is a continuous analytical function. Assume, therefore, that n is such a function of x , i.e.

$$n = f(x),$$

where x is the coordinate perpendicular to the surface of the liquid. We have also

$$f(-\infty) = 0,$$

and

$$f(+\infty) = n_1,$$

n_1 being taken as zero. Consider the force of attraction of the particles of the liquid on a particle at P in the surface of the liquid. Let the x coordinate of P be ξ , and consider a plate of liquid parallel to the surface at a distance h below P and of thickness dx . For the plate dx

$$x = \xi + h.$$

Firstly, figure 1, suppose that

$$h < \sigma.$$

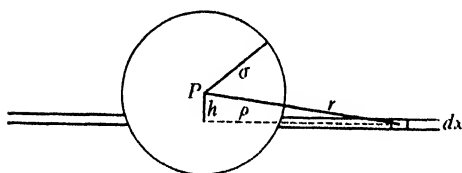


Figure 1.

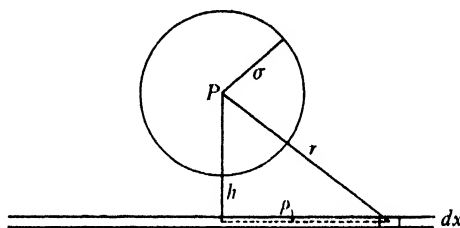


Figure 2.

The volume of a ring element dx of radius ρ is $2\pi\rho d\rho dx$, and this contains $2\pi f(\xi + h)\rho d\rho dx$ molecules. The coefficient of attraction being omitted, the force due to this element on the molecule at P , resolved perpendicularly to the surface of the liquid, is

$$2\pi f(\xi + h) \frac{\rho d\rho dx}{r^8} \times \frac{h}{r}.$$

Moreover

$$r^2 = \rho^2 + h^2,$$

$$\therefore r dr = \rho d\rho,$$

which gives the force due to the ring element as

$$2\pi f(\xi + h) h dx dr / r^8.$$

Therefore the total force F_1' on P due to the plate dx is given by

$$F_1' = 2\pi f(\xi + h) h dx \int_{r=\sigma}^{\infty} \frac{dr}{r^8}$$

$$= \frac{2\pi}{7\sigma^7} f(\xi + h) h dx \quad \dots\dots(11.1).$$

Secondly, figure 2, suppose that $h > \sigma$.

In this case the ring element is as before and the total force F_2' due to the slab is given by

$$\begin{aligned} F_2' &= 2\pi f(\xi + h) h dx \int_{r=h}^{\infty} \frac{dr}{r^3} \\ &= \frac{2\pi}{h^2} f(\xi + h) dx \end{aligned} \quad \dots\dots(11.2).$$

Thirdly, the total force downwards on the particle at P due to the attraction of all the molecules below a plane through P is given by

$$\frac{2\pi}{7} (F_1 + F_2),$$

where

$$F_1 = \int_{h=0}^{\sigma} \frac{f(\xi + h) h dh}{\sigma^7},$$

and

$$F_2 = \int_{h=\sigma}^{\infty} f(\xi + h) \frac{dh}{h^2},$$

since, in the equations (11.1) and (11.2), $dx = dh$, ξ being constant. This force is therefore

$$\frac{2\pi}{7} \left\{ \frac{1}{\sigma^7} \int_{h=0}^{\sigma} f(\xi + h) h dh + \int_{h=\sigma}^{\infty} f(\xi + h) \frac{dh}{h^2} \right\}.$$

Consider F_1 . Throughout the range of integration h is small, and we can put

$$f(\xi + h) = f(\xi) + hf'(\xi) + \frac{h^2}{2!} f''(\xi) + \dots + \frac{h^n}{n!} f^{(n)}(\xi + \theta\sigma),$$

a rapidly converging series, of which the terms after the first are relatively negligible.

$$\begin{aligned} \text{Hence } F_1 &= \frac{1}{\sigma^7} \int_{h=0}^{\sigma} \left[f(\xi) h dh + f'(\xi) h^2 dh + f''(\xi) \frac{h^3}{2!} + \dots \right] \\ &= \frac{1}{\sigma^7} \left[\frac{1}{2} \sigma^2 f(\xi) + \frac{1}{3} \sigma^3 f'(\xi) + \frac{\sigma^4}{4 \cdot 2!} f''(\xi) + \dots \right] \\ &= \frac{1}{2\sigma^5} f(\xi) + \frac{1}{3\sigma^4} f'(\xi) + \frac{1}{4\sigma^3 \cdot 2!} f''(\xi) + \dots \end{aligned} \quad \dots\dots(11.3).$$

Next consider F_2 . In the region beyond $h = \sigma$ we may imagine that within an interval from $h = \sigma$ to $h = \sigma + k$, where k is large compared with σ , the function $f(h)$ attains a value very nearly equal to n_1 , its value at infinity. Beyond the plane $h = \sigma + k$ the function $f(h)$ changes very slowly and is always less than n_1 .

$$\text{Hence } F_2 = \int_{h=\sigma}^k f(\xi + h) \frac{dh}{h^2} + R_2,$$

where

$$R_2 = \int_{h=k}^{\infty} f(\xi + h) \frac{dh}{h^2}$$

and

$$\begin{aligned} |R_2| &< \int_{h=k}^{\infty} n_1 \frac{dh}{h^2} \\ &< n_1 \int_k^{\infty} \frac{dh}{h^2} \\ &< \frac{n_1}{k}, \end{aligned}$$

which is negligible in comparison with the effect of the region next considered. In this region where $\sigma \leq h \leq k$,

$$f(\xi + h) = f(\xi) + hf'(\xi) + \frac{h^2}{2!}f''(\xi) + \dots + \frac{h^n}{n!}f^{(n)}(\xi + \theta h).$$

$$\therefore \int_{h=\sigma}^k f(\xi + h) \frac{dh}{h^6} = f(\xi) \int_{\sigma}^k \frac{dh}{h^6} + f'(\xi) \int_{\sigma}^k \frac{dh}{h^5} + \frac{f''(\xi)}{2!} \int_{\sigma}^k \frac{dh}{h^4} + \dots$$

$$= \frac{1}{5} f(\xi) \left(\frac{1}{\sigma^5} - \frac{1}{k^5} \right) + \frac{1}{4} f'(\xi) \left(\frac{1}{\sigma^4} - \frac{1}{k^4} \right) + \frac{1}{3 \cdot 2!} f''(\xi) \left(\frac{1}{\sigma^3} - \frac{1}{k^3} \right) + \dots$$

Since k is large compared with σ , and σ itself is very small we can put

$$F_2 = \frac{1}{5\sigma^5} f(\xi) + \frac{1}{4\sigma^4} f'(\xi) + \frac{1}{3\sigma^3 \cdot 2!} f''(\xi) + \dots \quad \dots\dots(11.4),$$

where the terms rapidly diminish in magnitude.

Fourthly, the total force upwards on the molecule at P due to the attraction of all the molecules above the plane through P is given by

$$\frac{2\pi}{7} (F_3 + F_4),$$

where

$$F_3 = \frac{1}{\sigma^7} \int_{h=0}^{\sigma} f(\xi - h) h dh,$$

$$= \frac{1}{2\sigma^6} f(\xi) - \frac{1}{3\sigma^4} f'(\xi) + \frac{1}{4\sigma^3 \cdot 2!} f''(\xi) - \dots \quad \dots\dots(11.5),$$

and

$$F_4 = \frac{1}{5\sigma^5} f(\xi) - \frac{1}{4\sigma^4} f'(\xi) + \frac{1}{3\sigma^3 \cdot 2!} f''(\xi) - \dots \quad \dots\dots(11.6).$$

Therefore, fifthly, the total resultant downwards force on the molecule at P due to all molecules above and below the plane through P is given by

$$\frac{2\pi}{7} F,$$

where

$$F = (F_1 - F_3) + (F_2 - F_4)$$

$$= 2 \left[\frac{1}{3\sigma^4} f'(\xi) + \frac{1}{5\sigma^2 \cdot 3!} f'''(\xi) + \dots \right] + 2 \left[\frac{1}{4\sigma^4} f'(\xi) + \frac{1}{2\sigma^2 \cdot 3!} f'''(\xi) + \dots \right]$$

$$= \frac{7}{6\sigma^4} f'(\xi) + \frac{7}{30\sigma^2} f'''(\xi) + \dots \quad \dots\dots(11.7),$$

in which expression all the terms except the first can generally be neglected.

Therefore, the total resultant downwards force on the molecule at P is

$$\frac{\pi}{3\sigma^4} f'(\xi) \quad \dots\dots(11.8).$$

The work done by the molecule in traversing the liquid from the interior to the vapour is, therefore,

$$- \frac{\pi}{3\sigma^4} \int_{+\infty}^{-\infty} f'(\xi) d\xi \quad \dots\dots(11.9)$$

$$= - \left[\frac{\pi}{3\sigma^4} f(\xi) \right]_{+\infty}^{-\infty}$$

$$= \frac{\pi n_l}{3\sigma^4} \quad \dots\dots(11.10),$$

since it may be assumed that at the two ∞ points $f''(\xi)$, $f^{iv}(\xi)$, etc., all vanish. This expression is the same as (8.6). Similarly, the transfer of momentum and kinetic energy depend only on the initial and final values of the density. However, in the above treatment we have neglected the effect of the transfer of momentum in collision on the work done by a molecule in escaping from the liquid. In a homogeneous fluid this effect is represented by the collision factor $v/(v-b)$. The effect in a medium of diminishing density is easily calculated.

In a homogeneous medium the work done by an escaping molecule must be multiplied by a collision factor F , where

$$F = (v-b)/v.$$

In each layer of the surface of a liquid of diminishing density the factor becomes F_1 , where

$$\begin{aligned} F_1 &= (v_1 - b)/v_1 \\ &= 1 - b/v_1, \end{aligned}$$

b being constant, and v_1 the molecular volume in the layer. Since

$$n = N/v$$

and

$$v_1 = N/n_1,$$

where, as before,

$$n_1 = f(\xi_1),$$

we have

$$F_1 = 1 - b \{f(\xi_1)\}/N,$$

and the total work done by a molecule in traversing the liquid from the interior to the vapour becomes W_v , where

$$W_v = -\frac{\pi}{3\sigma^4} \left[\int_{+\infty}^{-\infty} f'(\xi) d\xi - \frac{b}{N} \int_{+\infty}^{-\infty} f(\xi) f'(\xi) d\xi \right] \quad \dots\dots(11.11),$$

instead of being given by the expression (11.9). On integration,

$$\begin{aligned} W_v &= -\frac{\pi}{3\sigma^4} \left[f(\xi) - \frac{b}{2N} f^2(\xi) \right] \\ &= \frac{\pi\mu}{3\sigma^4} \left[n_1 - \frac{b}{2N} n_1^2 \right] \end{aligned}$$

Inserting the attraction coefficient μ and by means of equation (10.3), we have

$$\begin{aligned} W_v &= \frac{2K}{n_1} - \frac{b}{N} K \\ &= \frac{2Kv}{N} - \frac{Kb}{N} \\ &= \frac{2K}{N} \left(v - \frac{b}{2} \right) \quad \dots\dots(11.12). \end{aligned}$$

Thus in a fluid of continuously diminishing density the collision factor becomes

$$\frac{v}{v - \frac{1}{2}b},$$

and

$$n = \frac{N}{v - \frac{1}{2}b} \quad \dots\dots(11.13).$$

This factor does not affect the cohesion of a homogeneous liquid, but it does influence the vapour pressure. The same factor must also be introduced into the expression (10.11) for the surface tension because the new surface created is such a region of varying density.

Consequently we have
$$S = \frac{\pi \mu N^2}{24 \sigma^3 v^2} \cdot \frac{v - \frac{1}{2}b}{v} \quad \dots\dots(11.14);$$

and by comparison with equation (9.3) we have

$$K = \frac{4S}{\sigma} \cdot \frac{v}{v - \frac{1}{2}b} \quad \dots\dots(11.15)$$

$$= \frac{4.331S}{b^{\frac{1}{3}}} \cdot \frac{v}{v - \frac{1}{2}b} \times 10^8 \quad \dots\dots(11.16),$$

from equation (6.7). If the liquid is associated, σ must be multiplied by $A^{\frac{1}{3}}$ and b by A .

§ 12. THE VARIATION OF DENSITY THROUGH THE SURFACE OF A LIQUID

We are now in a position to calculate the density of the liquid at any point in the surface. Let ξ_1 be the coordinate of the point, n_1 the molecular density, v_1 the molecular volume, K_1 the cohesion and λ_1 the coefficient of the most probable speed of the particles of the liquid at this point. The work W_1 done by a particle in escaping to this point is given by

$$\begin{aligned} W_1 &= -\frac{\pi}{3\sigma^4} \left[f(\xi) - \frac{b}{2N} f^2(\xi) \right]_{+\infty}^{\xi_1} \\ &= \frac{\pi}{3\sigma^4} \left[n_1 - n_1 - \frac{b}{2N} (n_1^2 - n_1^2) \right] \\ &= \frac{2K_1}{N} \left(v_1 - \frac{b}{2} \right) - \frac{2K_1}{N} \left(v_1 - \frac{b}{2} \right) \quad \dots\dots(12.1). \end{aligned}$$

Also, from equation (7.8)

$$W_{\lambda_1} = \frac{1}{2} m P^2 (\lambda_1^2 - \lambda_1^2) \quad \dots\dots(12.2),$$

and from equation (7.10)

$$\frac{(v_1 - b) \lambda_1}{(v_1 - b) \lambda_1} = e^{-W_{\lambda_1} / \frac{1}{2} \lambda_1^2 \Theta}.$$

Now the value of λ_1 in any particular layer is given by the equation of state (6.10), which provides a means of eliminating λ_1 . Moreover, in the liquid state we may put $p=0$ as compared with K . So we get

$$\frac{\lambda_1}{\lambda_1} = \sqrt{\frac{(v_1 - b)(p + K_1)}{(v_1 - b)(K_1)}}.$$

And since, as we shall see, K is of the form a/v^2 , we obtain

$$\left(\frac{v_1 - b}{p + a/v_1^2} \right)^{\frac{1}{2}} = v_1 \left(\frac{v_1 - b}{a} \right)^{\frac{1}{2}} e^{W_{\lambda_1} / \frac{1}{2} \lambda_1^2 \Theta} \quad \dots\dots(12.3),$$

where all the terms except v_1 are known.

§ 13. ADAPTATION OF THE FORMULAE FOR CALCULATION

The formulae so deduced provide, for the first time, a practical means of calculating the physical properties of liquids and gases. For the attraction coefficient μ we have from equation (11.14)

$$\mu = \frac{24A^3\sigma^3Sv^3}{\pi N^2(v - \frac{1}{2}b)} \quad \dots\dots(13.1).$$

With the aid of equation (6.7), this becomes

$$\mu = \frac{36A^3bSv^3}{\pi^2N^2(v - \frac{1}{2}b)} \quad \dots\dots(13.2)$$

$$= 1.639A^3Sbv^3(v - \frac{1}{2}b)^{-1} \times 10^{-71} \quad \dots\dots(13.3).$$

For the value K_a in dynes per cm² of the cohesion K we obtain from equation (11.16)

$$K_a = 2.642 \times 10^{79} \mu A^{-\frac{1}{3}} b^{-\frac{1}{3}} v^{-2} \quad \dots\dots(13.41).$$

The value K_a in atmospheres per cm² is obtained by dividing by 1.013×10^6 , which gives

$$K_a = 2.608 \times 10^{73} \mu A^{-\frac{1}{3}} b^{-\frac{1}{3}} v^{-2} \quad \dots\dots(13.42).$$

Apart from the A , these formulae are of the form

$$K = a/v^2 \quad \dots\dots(13.5),$$

as was supposed by van der Waals, where

$$a = \frac{2.608\mu}{b^{\frac{1}{3}}} \times 10^{73} \quad \dots\dots(13.6),$$

its value now being known definitely. We have now all the material for adapting the gas equation and the vaporization formula (7.15). The former may be put into the form

$$p = \frac{\lambda^2 RT}{A(v-b)} - K \quad \dots\dots(13.7)$$

$$= 82.06 \frac{\lambda^2 T}{A(v-b)} - K \quad \dots\dots(13.8),$$

where 82.06 is the value of R , corresponding to the pressure in atmospheres, obtained by dividing the centigrade c.g.s. value by 1.0133×10^6 .

Coming now to the development of the vaporization formula, it is convenient for the time being to omit A . Thus we have

$$\begin{aligned} W_s &= W_v - W_\lambda \\ &= \frac{2K}{N} (v - \frac{1}{2}b) - \frac{1}{2}mP^2(\lambda^2 - 1) \quad \dots\dots(13.9) \end{aligned}$$

$$= \frac{2K(v - \frac{1}{2}b)(v-b)}{N(v-b)} - \frac{2}{3}\Theta(\lambda^2 - 1) \quad \dots\dots(13.10).$$

Putting $K(v-b) = \frac{2}{3}N\lambda^2\Theta$,(13.111),

since p is very small compared with K ,

$$W_s = \frac{4\lambda^2\Theta}{3(v-b)} \left(\frac{v-\frac{1}{2}b}{v-b} \right) - \frac{2}{3}\Theta(\lambda^2-1) \quad \text{.....(13.112)}$$

$$= \frac{2}{3}\Theta \left\{ 2\lambda^2 \left(\frac{v-\frac{1}{2}b}{v-b} \right) - \lambda^2 + 1 \right\} \quad \text{.....(13.12).}$$

Comparison with equation (7.12) gives

$$p = \frac{\lambda P\Theta}{v-b} \exp \left[-2 \left(\frac{v-\frac{1}{2}b}{v-b} \right) + 1 - 1/\lambda^2 \right] \quad \text{.....(13.13).}$$

By again making use of the relation

$$\lambda = \sqrt{\frac{K(v-b)}{P\Theta}} \quad \text{.....(13.14),}$$

in which p has been neglected as being very small compared with K , it is possible to remove λ completely from the vapour pressure formula. Thus from equation (11.16) we have

$$\lambda = 2.081 \times 10^4 \sqrt{\frac{Sv(v-b)}{b^{\frac{1}{2}}(v-\frac{1}{2}b)P\Theta}} = 2.281 \sqrt{\frac{Sv(v-b)}{b^{\frac{1}{2}}(v-\frac{1}{2}b)T}} \quad \text{.....(13.15),}$$

which gives

$$p = 2.081 \times 10^4 \sqrt{\frac{SvRT}{b^{\frac{1}{2}}(v-\frac{1}{2}b)(v-b)}} \exp \left[-2 \frac{v-\frac{1}{2}b}{v-b} + 1 - \frac{0.192T(v-\frac{1}{2}b)}{Sv(v-b)} \right] \quad \text{.....(13.16).}$$

Giving R and e^{-1} their numerical values 8.32×10^7 and 0.368 , respectively, we obtain the vapour pressure p_a in dynes per cm^2 as:

$$p_a = 6.99 \times 10^7 \sqrt{\frac{vST}{b^{\frac{1}{2}}(v-b)(v-\frac{1}{2}b)}} \exp \left[-\frac{v-\frac{1}{2}b}{v-b} \left\{ 2 + \frac{0.192Tb^{\frac{1}{2}}}{Sv} \right\} \right] \quad \text{.....(13.17).}$$

It is convenient to have this equation in the forms which give the values p_a , and p_{mm} of the vapour pressure in atmospheres and in millimetres of mercury respectively. These are obtained by dividing the equation by 1.016×10^6 and by multiplying the result by 760. Thus, introducing the association factors A_g and A_l , we obtain finally

$$p_a = 68.8 \sqrt{\frac{v_l S T A_g}{b^{\frac{1}{2}} A_l^{\frac{1}{2}} (v_l - b) (v_l - \frac{1}{2}b)}} \exp \left[-\frac{v_l - \frac{1}{2}b}{v_l - b} \left\{ 2 + \frac{0.192 T b^{\frac{1}{2}}}{S v_l A_l^{\frac{1}{2}}} \right\} \right] \quad \text{.....(13.18)}$$

$$p_{mm} = 5.16 \times 10^4 \sqrt{\frac{v_l S T A_g}{b^{\frac{1}{2}} A_l^{\frac{1}{2}} (v_l - b) (v_l - \frac{1}{2}b)}} \exp \left[-\frac{v_l - \frac{1}{2}b}{v_l - b} \left\{ 2 + \frac{0.192 T b^{\frac{1}{2}}}{S v_l A_l^{\frac{1}{2}}} \right\} \right] \quad \text{.....(13.19).}$$

It will be seen that these formulae contain no unknown quantities except b and A . If we work with unassociated liquids, A can be neglected, leaving only b .

The sequel will show that b is constant except for a very small temperature contraction, which is compatible with a nearer mean distance of approach of the faster moving molecules at higher temperatures.

By taking into account the effects of the different attractions of two sets of molecules, it is obvious that the method can be applied to the solubility of gases in liquids and the miscibility of liquids. There is, however, a new effect in this connexion that will have to be considered, namely the effect of a foreign molecule on the cohesion and molecular volume of a liquid. When a molecule of solute, with, e.g., a smaller field of force than that of the solvent molecules, enters the solvent, the solute molecule must push apart the solvent molecules against their greater attraction, and vice versa. This means a change of molecular volume. The effect, which was indicated in a previous paper, is due to the difference in the attraction coefficients of the two sets of molecules. It is the reason why a liquid with less cohesion may not mix completely with another whose cohesion is greater. Actually the liquid with less cohesion is squeezed out of the denser liquid.

Similarly it is clear that the formulae can also be applied to the explanation of osmotic pressure. These phenomena will be treated in a subsequent paper. As an example of the wide application of the method, the theoretical part of this paper will be concluded by a discussion of the viscosity of liquids.

§ 14. THE VISCOSITY OF FLUIDS

This is particularly interesting as an instance of the fundamental importance of the collision factor, which, as will be seen, supplies the reason for the negative temperature coefficient of the viscosity of liquids. In dealing with viscosity, the force measured is that exerted between a moving fluid and a stationary solid. Momentum is transferred from the fluid to the solid through the adsorbed layer of intermediate density which must exist at the liquid-solid interface. As in previous sections, it is assumed that molecules behave as perfectly elastic attracting spheres. Collision takes place between individual molecules, whether the medium be gaseous, liquid or solid. At each collision the transfer of momentum obeys the ordinary laws of dynamics and molecules reflected from molecules forming the solid surface have such velocities as result from these laws.

Suppose the fluid to be moving with the mass velocity \bar{u} in the direction OX , figure 3. We have to find the average momentum of the molecules crossing a plane $z=\zeta$ in the adsorbed layer between the homogeneous fluid and the stationary bounding solid, whose surface OX is at the plane $z=0$. The number of molecules crossing unit area of the plane $z=\zeta$ from the direction of the solid per second is

$$\frac{1}{2}n\bar{c} \quad \dots\dots(14.1),$$

where n is a function of z , say $n=f_1(z)$ (14.2),

and \bar{c} is given by $\bar{c}=4\sqrt{\frac{\lambda^2\Theta}{3\pi m}}\cdot\frac{v}{v-b}$ (14.3).

Now, as before,

$$\lambda^2 = \frac{K(v-b)}{P_0} \quad \dots\dots(14.4).$$

$$\therefore \bar{c} = 2\sqrt{2} \cdot \left(\frac{Kv^2}{\pi M(v-b)} \right)^{\frac{1}{2}} \quad \dots\dots(14.5)$$

$$= f_2(z), \text{ say} \quad \dots\dots(14.6).$$

The average mass velocity \bar{u} in the direction OX of molecules crossing the plane $z=\zeta$ in both directions is also a function of z , or

$$\bar{u} = f_3(z) \quad \dots\dots(14.7).$$

O

N

Figure 3.

Moreover, in treatises on the kinetic theory it is shown that the molecules crossing the plane $z=\zeta$ come from an average distance $\frac{2}{3}l$, where l is the mean free path and is given by the equation

$$l = \frac{1}{\sqrt{2} \cdot \pi n \sigma^2} \quad \dots\dots(14.8).$$

or,

$$l = f_4(z) \quad \dots\dots(14.9).$$

But on account of the change in density of the fluid in the direction at right angles to the plane $z=\zeta$, the mean free path is different on different sides of the plane. Thus if l_{21} and l_{23} are the mean free paths in the directions of the liquid-solid interface and the pure liquid, respectively,

$$l_{23} > l_{21}.$$

The evaluation of these magnitudes, and their introduction into the equations of motion, leads to complications that it is impossible to consider in the present paper. It should be noticed, however, that, at both limits of integration the mean

free paths are the same in both directions. Consequently, the omission of these details may not affect the result considerably. Returning to the argument, we note that the average momentum in the direction OX of a molecule in the plane $\zeta - \frac{2}{3}l_{21}$ is

$$mf_3(\zeta - \frac{2}{3}l_{21}) \quad \dots\dots(14.10).$$

So that the total directed momentum per second carried across unit area of the plane $z=\zeta$ from the direction of the solid is

$$\frac{1}{4}mf_1(\zeta)f_2(\zeta)f_3(\zeta - \frac{2}{3}l_{21}) \quad \dots\dots(14.11).$$

Similarly the directed momentum per unit area carried across the plane by all the molecules crossing from the direction of the pure liquid is

$$\frac{1}{4}mf_1(\zeta)f_2(\zeta)f_3(\zeta + \frac{2}{3}l_{23}) \quad \dots\dots(14.12).$$

Since the directed momentum in the plane $z=\zeta$ is constant, the total momentum added from one side must be as much greater than the average for the plane as that added from the other side in less than the average momentum of the plane $z=\zeta$. This relation holds for each plane throughout the adsorbed layer until we reach the surface of the solid, which is a plane of no momentum. Here particles reaching the surface with the average momentum corresponding to the plane at a distance of two-thirds of one free path from it, are reflected from the surface with an equal momentum in the opposite direction. It is evident, therefore, that the surface may be supposed to act in the manner of a mirror, as is assumed frequently in problems of attraction, and the solid may be replaced by an imaginary fluid with diminishing density moving in the opposite direction and corresponding exactly to the mirror image of the adsorbed layer and the real fluid. The surface of the solid must be taken as that plane where the density is midway between that of the liquid and that of the solid.

We return now to the expressions (14.11) and (14.12). The former represents the total momentum per unit area added to the plane per second from one side, while the only molecules to which it is added come from the other side. Consequently the force acting on these molecules is represented by the difference between the expressions (14.11) and (14.12). This force X is equal to

$$X = \frac{1}{4}mf_1(\zeta)f_2(\zeta)\{f_3(\zeta + \frac{2}{3}l_{23}) - f_3(\zeta - \frac{2}{3}l_{21})\} \quad \dots\dots(14.13)$$

$$= \frac{1}{4}mf_1(\zeta)f_2(\zeta)f_3'(\zeta)\{\frac{2}{3}l_{23} + \frac{2}{3}l_{21}\} \quad \dots\dots(14.14).$$

Ignoring the inequality in the values of l , this last equation becomes

$$X = \frac{1}{3}mf_1f_2f_3'f_4 \quad \dots\dots(14.15).$$

Now, from Newton's law, we have

$$\frac{X}{A} = \kappa \frac{d\bar{u}}{dz} \quad \dots\dots(14.16).$$

And, since $A=1$, we find that

$$X = \kappa f_3' = \frac{1}{3}mf_1f_2f_3'f_4,$$

or

$$\kappa = \frac{1}{3}mf_1f_2f_4 \quad \dots\dots(14.17)$$

$$= f(n) \quad \dots\dots(14.18),$$

since f_1 , f_2 and f_4 are all functions of n .

This expression shows that the value of κ in any plane parallel to the direction of flow depends on the average density and molecular diameter in that plane.

But in an experimental determination we measure the average effect of the transfer of momentum from the homogeneous liquid through the adsorbed layer to the surface of the solid. An average value $\bar{\kappa}$ of the viscosity is obtained by multiplying both sides of equation (14.17) by dn , integrating from $n = n_{sl}$ to $n = n_l$, and dividing by the integral of dn between the same limits. This gives the observed viscosity

$$\eta = \bar{\kappa} = \int_{n=n_{sl}}^{n_l} f(n) dn / \int_{n=n_{sl}}^{n_l} dn \quad \dots\dots(14.19).$$

To evaluate this expression we have

$$f(n) = \frac{2}{3} \frac{m}{\pi \sigma^2} \left\{ \frac{K v^2}{\pi M (v-b)} \right\}^{\frac{1}{2}} \quad \dots\dots(14.20)$$

$$= \frac{2}{3} \frac{M^{\frac{1}{2}}}{\pi^{\frac{3}{2}} N} \left\{ \frac{K v^2}{\sigma^4 (v-b)} \right\}^{\frac{1}{2}}$$

$$= \frac{2}{3} \frac{M^{\frac{1}{2}}}{\pi^{\frac{3}{2}} N} \left\{ \frac{a}{\sigma^4 (v-b)} \right\}^{\frac{1}{2}} \quad \dots\dots(14.21)$$

$$= D \left(\frac{1}{v-b} \right)^{\frac{1}{2}} \quad \dots\dots(14.22),$$

where D is a constant. Therefore the integral in the numerator of equation (14.19) depends on

$$I = \int \left(\frac{1}{v-b} \right)^{\frac{1}{2}} dn,$$

since the other terms may be taken as constant.

Now

$$n = \frac{N}{v}$$

and

$$dn = -\frac{N}{v^2} dv,$$

so that

$$I = - \int \frac{dv}{(v-b)^{\frac{1}{2}} v^2}.$$

By means of the substitution

$$v-b=y^2$$

we get

$$I = -2 \int \frac{dy}{(y^2+b)^2},$$

and by putting

$$y^2+b=r^2$$

we have

$$I = -2 \int \frac{dy}{r^4}.$$

This can be integrated by means of the formula

$$2b \int \frac{dy}{r^4} = \frac{y}{r^2} + \int \frac{dy}{r^2},$$

which gives

$$I = - \left\{ \frac{y}{b(y^2 + b)} + \frac{1}{b^{\frac{3}{2}}} \tan^{-1} \frac{y}{b^{\frac{1}{2}}} \right\}$$

$$= - \left\{ \frac{(v-b)^{\frac{1}{2}}}{bv} + \frac{1}{b^{\frac{3}{2}}} \tan^{-1} \left(\frac{v-b}{b} \right)^{\frac{1}{2}} \right\}.$$

Consequently

$$\eta = D \frac{\frac{(v-b)_i^{\frac{1}{2}}}{bv_i} + \frac{1}{b^{\frac{3}{2}}} \tan^{-1} \left(\frac{v-b}{b} \right)_i^{\frac{1}{2}} - \frac{(v-b)_{sl}^{\frac{1}{2}}}{bv_{sl}} - \frac{1}{b^{\frac{3}{2}}} \tan^{-1} \left(\frac{v-b}{b} \right)_{sl}^{\frac{1}{2}}}{N \left\{ \frac{1}{(v-b)_{sl}} - \frac{1}{(v-b)_i} \right\}} \dots\dots(14.23).$$

When the properties of mixtures are treated in a subsequent paper, it will be shown that

$$\bar{\sigma} = \frac{\bar{m}^{\frac{1}{2}}}{\bar{n}} \left(\frac{n_1}{m_1^{\frac{1}{2}}} \sigma_1 + \frac{n_2}{m_2^{\frac{1}{2}}} \sigma_2 \right)$$

and

$$\bar{b} = \frac{2}{3} \pi \bar{\sigma}^3 N$$

$$= \frac{2}{3} \pi N \left\{ \frac{n_1}{\bar{n}} \left(\frac{\bar{m}}{m_1} \right)^{\frac{1}{2}} \sigma_1 + \frac{n_2}{\bar{n}} \left(\frac{\bar{m}}{m_2} \right)^{\frac{1}{2}} \sigma_2 \right\}$$

With the aid of these expressions, together with (9.11) and (10.6), the above formula for the viscosity can be evaluated in the manner which follows. As will be seen, however, the application depends on a knowledge of K , v and b in the solid state. Conversely the formula could be used to determine the most probable values of these quantities by making use of available viscosity data extending over a wide range. The investigation is, however, too elaborate for this preliminary paper.

A simple and more manageable formula for the viscosity may be deduced by multiplying both sides of equation (14.17) by $f'(n)$, integrating as before and dividing by the integral of $f'(n)$ between the same limits. This gives

$$\eta = \bar{\kappa} = \frac{\int_{n=n_{sl}}^{n_i} f(n) f'(n)}{\int_{n=n_{sl}}^{n_i} f'(n)}$$

$$= \frac{1}{2} \{f(n_{sl}) + f(n_i)\} \dots\dots(14.24).$$

To evaluate η we have

$$f(n) = \frac{2}{3} \frac{M^{\frac{1}{2}}}{\pi^{\frac{3}{2}} N} \left\{ \frac{Kv^2}{\sigma^4 (v-b)} \right\}^{\frac{1}{2}}$$

$$= GM^{\frac{1}{2}} F^{\frac{1}{2}}, \dots\dots(14.25),$$

where

$$G = \frac{2}{3} \pi^{\frac{1}{2}} N$$

$$= 1.98 \times 10^{-25} \dots\dots(14.26),$$

and

$$F = \left\{ \frac{Kv^2}{\sigma^4 (v-b)} \right\} \dots\dots(14.27).$$

Viscosity of a liquid. In this case we may write

$$f(n)_{sl} = f(n)_s^{\frac{1}{2}} f(n)_l^{\frac{1}{2}},$$

when we get

$$\eta_l = \frac{GM^{\frac{1}{2}}}{2} F_l^{\frac{1}{2}} (F_s^{\frac{1}{2}} + F_l^{\frac{1}{2}}),$$

where F_s is nearly constant for the material of the apparatus, since the temperature coefficient in the solid state is small compared with that in the liquid condition. Now, since

$$\begin{aligned} \sigma^{\frac{1}{2}} &= \left(\frac{3b}{2\pi N} \right)^{\frac{1}{2}} \\ &= \frac{4.331S}{b^{\frac{1}{2}}} \cdot \frac{v}{v - \frac{1}{2}b} \times 10^8, \end{aligned}$$

the factor

$$\begin{aligned} F_l &= 4.33 \left(\frac{2\pi N}{3} \right)^{\frac{1}{2}} \times 10^8 \cdot \frac{Sv^3}{b^{\frac{1}{2}}(v-b)(v-\frac{1}{2}b)} \\ &= H \left\{ \frac{Sv^3}{b^{\frac{1}{2}}(v-b)(v-\frac{1}{2}b)} \right\} \end{aligned}$$

where

$$H = 6.00 \times 10^{40} \quad \dots\dots(14.28).$$

Thus the viscosity of a liquid becomes

$$\begin{aligned} \eta_l &= \frac{GH^{\frac{1}{2}}M^{\frac{1}{2}}}{2} \left\{ \frac{Sv^3}{b^{\frac{1}{2}}(v-b)(v-\frac{1}{2}b)} \right\}_l^{\frac{1}{2}} \left[\frac{F_s^{\frac{1}{2}}}{H^{\frac{1}{2}}} + \left\{ \frac{Sv^3}{b^{\frac{1}{2}}(v-b)(v-\frac{1}{2}b)} \right\}_l^{\frac{1}{2}} \right] \\ &= 2.41 \times 10^{-6} M^{\frac{1}{2}} \left\{ \frac{Sv^3}{b^{\frac{1}{2}}(v-b)(v-\frac{1}{2}b)} \right\}_l^{\frac{1}{2}} \left[\left\{ \frac{Sv^3}{b^{\frac{1}{2}}(v-b)(v-\frac{1}{2}b)} \right\}_l^{\frac{1}{2}} + B_l \right] \\ &\quad \dots\dots(14.29), \end{aligned}$$

where

$$B_l = F_s^{\frac{1}{2}}/H^{\frac{1}{2}} \quad \dots\dots(14.30),$$

and is practically constant for the material of the apparatus with a most probable value of 6.20. The form of this factor is important, because eventually it should be possible to use it in calculating the values of K and b in the solid state.

Viscosity of a gas. To calculate this we have

$$\eta_g = \frac{1}{2} (f_{lg} + f_g),$$

where the subscript lg refers to the fact that the greatly superior attraction of the solid particles must bring about the condensation of the gas at the solid surface in a state comparable to the liquid condition. Presumably this adsorbed layer is not more than one or two molecules in thickness, so that the measured diameter of the capillary tube is not affected. But the motion communicated to this condensed layer by the molecules of the gas which strike it will be inappreciable in comparison with that of the gas. Therefore the adsorbed layer and not the surface of the solid must be taken as the limit of integration in this direction. In the case of a gas we may write

$$f(n)_{lg} = \frac{f(n)_l + f(n)_g}{2}$$

and the above expression may be written

$$\eta_0 = \frac{1}{2} \left\{ \frac{f_1}{\lambda} \right\}$$

Now, since λ and $v/(v-b)$ become equal to unity in the gaseous state,

$$\begin{aligned} f(n)_0 &= \left(\frac{2}{3} \right)^{\frac{1}{2}} \frac{R^{\frac{1}{2}} M^{\frac{1}{2}}}{N^{\frac{1}{2}} \pi^{\frac{1}{2}}} \left\{ \frac{T}{b^{\frac{1}{2}}} \right\}^{\frac{1}{2}} \\ &= J \left\{ \frac{T}{b^{\frac{1}{2}}} \right\}^{\frac{1}{2}}, \end{aligned} \quad \text{.....(14.31)}$$

where

$$J = 2.11 \times 10^{-5} \quad \text{.....(14.32),}$$

and, since

$$f(n)_1 = GH^{\frac{1}{2}} M^{\frac{1}{2}} \left\{ \frac{Sv^3}{b^{\frac{1}{2}} (v-b) (v-\frac{1}{2}b)} \right\}_1^{\frac{1}{2}},$$

we have

$$\begin{aligned} \eta_0 &= \frac{3}{4} JM^{\frac{1}{2}} \left[\left\{ \frac{T}{b^{\frac{1}{2}}} \right\}^{\frac{1}{2}} + \frac{GH^{\frac{1}{2}}}{3J} \left\{ \frac{Sv^3}{b^{\frac{1}{2}} (v-b) (v-\frac{1}{2}b)} \right\}_1^{\frac{1}{2}} \right] \\ &= 1.60 \times 10^{-5} M^{\frac{1}{2}} \left[\left\{ \frac{T}{b^{\frac{1}{2}}} \right\}^{\frac{1}{2}} + B_0 \left\{ \frac{Sv^3}{b^{\frac{1}{2}} (v-b) (v-\frac{1}{2}b)} \right\}_1^{\frac{1}{2}} \right] \quad \text{...(14.33),} \end{aligned}$$

where

$$\begin{aligned} B_0 &= \frac{GH^{\frac{1}{2}}}{3J} \\ &= 0.80 \quad \text{.....(14.34).} \end{aligned}$$

When the values of b , v and K have been ascertained for the solid state, it will be possible to calculate the exact density of the condensed gas in the adsorbed layer. In the meantime, having regard to the comparatively enormous attraction of the solid, the most probable value of the density of the adsorbed layer is that of the liquefied gas at its melting point. By means of this supposition it is possible to calculate the value of $f(n)_1$ and, therefore, of the viscosity of a gas. It will be seen that the agreement between the calculated and observed values is very good.

In considering the viscosity of liquids, that of mercury is of peculiar interest. It has long been felt that the observed values obtained from experiments in glass tubes were too low. From the above analysis it is evident that if mercury slips through glass tubes the liquid-solid interface cannot be a surface of no motion, and therefore that the viscosity of mercury cannot be measured in this way. Tamann and Hinnüber recognized this fact and employed amalgamated copper tubes. The values calculated from the above formulae agree with their results and not with the figures resulting from experiments in glass tubes. Erk attempted to overthrow Tamann and Hinnüber's contention by suggesting that the increased viscosity was due to the formation of crystals of amalgam in the tube. But this supposition is incompatible with the fact that constant values were obtained. The theoretical considerations now adduced show that Tamann and Hinnüber were right, and supply an explanation of the anomalous low values of the viscosity of mercury obtained in glass tubes. The values of the calculated viscosities quoted in table 2

are correct within about 10 per cent throughout the enormous range from the lightest gas to the heaviest liquid. It will be seen that the viscosity of gases increases with temperature, as required, while the opposite effect is obtained for liquids, in accordance with observation.

§ 15. APPLICATIONS OF THE THEORY

The theory developed in the preceding pages affords a clear insight into the general behaviour of the ultimate particles, of which real gases and liquids are composed. By its means we are enabled to picture the manner in which the complicated motions and interactions of these ultimate particles produce, in the aggregate, the physical effects which we observe as the everyday properties of fluids. In order to test the theory, a few substances have been chosen for their likelihood of being least associated, since it is impossible to determine association in the liquid state at present. The substances cover all types of bodies, elementary and compound, organic and inorganic, polar and non-polar, and range from the lightest gas to the heaviest liquid. The closeness of the agreement between the calculated values and those obtained by experiment revealed in the following tables can only be described as remarkable.

(1) *Vapour pressure.* In table 1 are given the values of b calculated from the vapour pressure equation.

Table 1. Vapour pressures of liquid substances

Substance	Temperature T	Molecular weight M	Density ρ	Molecular volume v	Surface tension S	Apparent volume b of the molecules	Association of vapour A	Vapour pressure p (mm.)
Hydrogen	15	2.016	0.0761	26.49	2.83	21.86	1.024	94.4
	20		0.0712	28.72	1.98	20.49	1.056	690
Ethyl ether	273	74.08	0.7363	100.6	19.1	85.5	1.016	185
	307.8		0.6960	106.4	14.7	84.8	1.029	760
n hexane	273	86.02	0.6787	126.9	20.5	111.0	1.010	46
	341		0.6148	140.1	13.4	110.8	1.032	745
Chloroform	298	119.5	1.476	80.97	26.2	69.3	1.014	203
	333.2		1.414	84.46	21.8	68.8	1.027	760
Phosphorus trichloride	273	137.4	1.613	85.21	29.3	75.5	1.006	38
	348.1		1.475	93.17	21.9	75.8	1.027	760
Mercury	373	200.6	13.35	15.03	452	14.14	1.000	0.30
	573		12.88	15.57	406	14.00	1.003	249

It will be seen that the values of b needed to give the observed vapour pressures are constant within 1 per cent, or less, except in the case of hydrogen. This is the first time that an equation of state has given constant values of b . It can hardly be doubted that the rather greater change in b calculated for hydrogen, is due in part to the difficulties of manipulation at very low temperatures, e.g. leakage of air. Moreover, the great change in the cohesion of liquid hydrogen, from 3.88×10^8 at 15° to 7.13×10^8 at 20° K., suggests that this substance may be greatly associated at the lower temperature, which is actually only just above its freezing point. It

may be that the 8th-power law of attraction does not hold at very low temperatures. We need to know the physical cause of the law. It is also noteworthy that whereas b shows a slight contraction with rise of temperature in other cases, for phosphorus trichloride a small expansion is observed. This anomaly is almost certainly due to experimental difficulties, for the single determination of the surface tension made by Ramsay and Shields, i.e. 28.71 at 16.4° , does not fit the plotted results obtained by Jaeger which were used in this calculation.

The figures quoted in the above table demonstrate the fact that the vapour pressures and boiling-points of liquids are the results of molecular attraction, volume and motion alone; and since b can be determined by other means, e.g. from the viscosity equation, the vapour pressures and boiling-points of liquids can be calculated directly from first principles.

(2) *The {pressure, volume, temperature} relations of gases, and the correction of the thermometer.* The gas equation

$$A(p + K)(v - b) = \lambda^2 RT,$$

contains two essential factors, A and λ , which were overlooked by van der Waals, and replaces his equation for the {pressure, volume, temperature} relations of gases. It is evident that the inclusion of these two factors suffices to give an account of these relationships, without variation of the apparent volume b of the molecules. In this formula the function K can now be calculated, and b is known from the vapour pressure formula, or otherwise. There remain the factors A and λ . An expression for calculating A will be communicated shortly. However, the latter factor is an implicit function of the other variables in the expression, and it can only be said that its value is the value which fits the equation. In the course of time, when a means has been found of calculating exactly the factor F , in the viscosity equation, it will be possible to use this equation or that relating to another property of gases for calculating λ . We shall then have a means of completely determining the {pressure, volume and temperature} relations of gases and vapours.

(3) *Viscosity.* Table 2 gives the viscosities of the range of substances considered in this paper calculated by means of the formula (14.29) and (14.33), together with the observed values.

Table 2. Viscosities of gases and liquids

Substance	Temperature	Viscosity	
		Calculated	Observed
Hydrogen	273	0.000088	0.000087
	373	0.000096	0.000100
Ether	273	0.0032	0.0029
	307.8	0.0027	0.0023*
<i>n</i> hexane	273	0.0035	0.0040
	341	0.0026	0.0022*
Chloroform	298	0.0048	0.0054
	333	0.0039	0.0041*
Mercury	373	0.033	0.034*
	537	0.028	

Extrapolated values.

It will be seen that the agreement between the calculated and observed values is sufficient to show that the viscosities of fluids can be calculated directly from first principles by means of the procedure developed in the present paper.

The methods of this paper can be applied to the whole field of molecular physics. The special case of water has not been treated here, because of its molecular complexity, but it is evident that it can be unravelled by the simultaneous consideration of several physical properties. It will then be possible to study the theory of solutions and steam. A preliminary investigation of the former has shown already that the depressions of the freezing points and the elevation of the boiling points of solutions of salts are due exactly to the greater attraction of the solid particles.

Throughout this paper the analysis has been made as simple as possible, in order to keep clearly in view the essential physical facts. For if these are obscured the most rigorous analysis can be of no utility. The central ideas have been the essential discontinuity of matter and molecular attraction.

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DISCUSSION

Prof. W. WILSON: The author arrives at the conclusion "that the average velocity of a molecule of a real substance is greater, and in the case of liquids and solids very much greater, than in an ideal gas". I am sure he has in mind the case where the molecule of the real substance has the same mass as the molecule of the ideal gas, and so he violates the principle of equipartition. Now I maintain that this principle is an inevitable consequence of the classical premises from which he professes to start out.

He is mistaken in supposing his definition of temperature (4.1) to be new. He will find a more complete statement of the same definition in the chapter on temperature in Max Planck's *Thermodynamik* and also in my work on *Theoretical Physics*, **1**, 223.

My last criticism is a minor one. The dimensional equation (4.3) is erroneous. There is in it an error of precisely the same type as that contained in

$$Q = M^{\frac{1}{2}} L^{\frac{1}{2}} T^{-1},$$

where Q , M , L and T are respectively electric charge, mass, length and time.

Prof. ANDRADE: I have been much impressed by the care and labour which the author has put into his ambitious attempt to build up an embracing theory of fluids. I am still of the opinion that the right way of approaching liquids is from the solid, rather than from the gaseous, point of view, but no doubt valuable work can be done from the latter aspect. There are, however, one or two points about the paper that trouble me considerably. It seems to me that the author's fundamental assumption, "that the average velocity of a molecule of a real substance is greater, and in the case of liquids and solids very much greater, than in an ideal gas", leads at once to grave difficulties, especially in view of his acceptance of the Maxwellian distribution law. Both Maxwell's law and the equipartition of energy follow from classical mechanics, on which, I understand, the author bases his theory. Yet if we accept the equipartition of energy his fundamental assumption is impossible. It would, for instance, lead to a value of the molecular specific heat for solids and liquids very much in excess of the experimental values. In any case, I see no reason for the statement that the velocities of molecules passing through a force-free point must be the same as in an ideal gas. The velocity in a force-free space is, of course, entirely dependent on the previous history of the particle.

I further find difficulties in his whole treatment of liquid viscosity. There is no doubt that there is no slip of a liquid at a solid surface, even in the case of liquids which do not wet the solid. Very extensive experiments have been carried out on this point. To take the case of mercury, which he quotes in particular, determinations of the viscosity by the flow through glass capillaries have been made by at least six observers, all of whom assume Poiseuille's law with no slip, and arrive at about the same value for the viscosity. The radii of the tubes used in the different experiments vary from 0.053 to 0.406 mm. If there were actually slip the values given by applying Poiseuille's law would show a large and systematic variation with radius. Bénard, in particular, in his measurements on mercury, went carefully into the question of an upper limit for the slip and showed that, even if it existed, it must be equivalent to something less than an increase of the diameter of the tube of 0.001 mm., which is, of course, beyond the limits of the measurement of radius.* Further, Fawsitt made measurements by a completely different method, namely that of the oscillating disc, using four different discs, of two different materials, and obtained values which not only were self-consistent, but also agreed very well with the capillary-tube values. If there were slip, these values, based on formulae which assume no slip, could not possibly show this degree of agreement. There seems no doubt that the values of Tammann and Hinnüber, carried out with a copper tube, were vitiated by the silting up of the tube in some way as a result of the action of the mercury on the copper, leading to the growth of either crystals or a sheet of amalgam.

If, now, we accept the consistent values found for glass capillaries and for iron and glass oscillating discs, we must substitute for the values which the author gives as "observed for mercury" viz. 0.034 and 0.025, at 100° C. and 264° C. respectively, other values, namely, 0.0124 and 0.0098, which are about a third of his calculated values. Further, the temperature coefficient of liquid viscosity given by his formula

* Brillouin, *Leçons sur la Viscosité*, 1, 158.

differs greatly from the experimental values. Another point that troubles me is the increase with temperature of the association of all the vapours given in his table 1. This seems very hard to reconcile with current ideas.

Returning to the question of slip at solid surfaces, there seems no reason why, quite apart from the experimental results, lack of wetting should imply slip. Slip is, after all, a question of the liquid-solid interface, while wetting further involves a gas surface. As a matter of fact Dr Greenland has shown, in my laboratory, that perfectly pure mercury does wet clean quartz glass. The fact that a mercury seal can preserve a vacuum unchanged for years seems conclusive proof that there is no faulty contact between the mercury and the glass. A very simple experiment that I have just carried out makes the lack of slip visible at once. A flat drop of mercury is put on a glass plate and a little dust is sprinkled on it. If the plate is then inclined, the drop will run down it, and from the dust it can be seen that this motion takes place by the mercury at the top of the drop running forward, while that in contact with the glass remains at rest.

If, however, I am unable to accept the author's treatment of liquid viscosity, in which, apparently, the interaction between the liquid and the solid surface plays so prominent a part, it is not to say that I do not find his paper very suggestive as to lines along which results may be sought.

Dr H. CHATLEY: This paper attempts to realize an ambition which I myself aimed at in my six papers on cohesion and molecular force presented to the Society. The whole question is whether or not a parabolic force formula can be made the basis of a theory of matter. Edser considered such a formula to be only a statistical and empirical generalization, and it may be questioned whether the author has really done more than confirm Edser's views. The author's basic equation of state includes three unknowns A , b and λ and so permits a considerable degree of discretionary adjustment to data. What view does the author take of the force law, within what range is it sufficiently exact, how can it be related to the actual multipolar structure of the molecules and their rotations, and how can its application to the solid state be envisaged?

AUTHOR's reply. In regard to Prof. Andrade's opinion that the subject is best approached from the point of view of solids, I would point out that the method adopted is a general one and should apply to gases, liquids and solids. The paper is an attempt to calculate the properties of matter from attraction, volume and motion. However, there can hardly be any doubt that both liquids and gases differ from solids in possessing an additional degree of freedom. The molecules are able to rotate. The law of force adopted applies to this state, and it may not apply to the solid state, in which the orientation of the particles is more or less fixed. The assumption of a greater average kinetic energy of the molecules of a real substance is essential to the paper. Equipartition is a consequence of Maxwell's law of distribution and holds only for a perfect gas. I maintain that molecular forces must alter the average kinetic energies of the molecules. At the same temperature, the mean kinetic energies of the molecules of different substances, or phases of substances, are different, according to the molecular forces existing. If this is true,

the law of equipartition falls to the ground. My theory is based on Maxwell's law of distribution, with the addition of this necessary consequence of Newton's laws of force. It is therefore truly classical in its basis. This answers Prof. Wilson's criticism also.

Prof. Andrade's contention that the velocities of molecules passing through transitory force-free points are not necessarily the same as they would be in an ideal gas of the same molecular weight appears to be sound. The statement in my paper was quoted from Kleeman's paper⁽⁴⁾. It is not essential to my thesis.

The theory does not necessarily lead to higher values of the specific heats of metals, because the principle of equipartition does not hold.

The explanation of the difficulty in regard to the viscosity of mercury is simple. Calculations of slip are based on empirical hydrodynamical considerations of internal friction, etc., which take no account of the discontinuity of matter or of the various effects of molecular attraction discussed in this paper. The actual effects on the radii of the tubes are due to thin adsorbed films, probably not of great thickness, and quite beyond the range of physical measurement. The fact that the observations involving slip in tubes of different diameter give consistent results is not necessarily a contradiction of my theory. The experiment which Prof. Andrade describes proves that the surface of a drop of mercury in contact with a glass plate moves less slowly than the drop. According to my theory, there is a very strong attraction between the molecules of the two substances, which ensures very close contact, if allowed. Even slight irregularities would produce the effect observed. Actually the mercury is rolling in adsorbed filth. In a capillary tube the effect need not be the same. This attraction of the particles is the cause of the sealing effect of mercury referred to. Molecules of air can penetrate between the glass-mercury interface only by possessing sufficient energy to overcome the cohesion of the surfaces, which they practically never do.

The considerations which I have introduced into the discussion of viscosity are the necessary result of molecular attraction. The formula developed is approximate but I have shown how a more accurate formula may be deduced. Doubtless further modifications will be found to be necessary. But this is the first time that the observed viscosities of liquids, with temperature coefficients of the right sign, have been calculated from first principles. I prefer to accept the values of the viscosity of mercury indicated by my theory as giving the explanation of a long-felt difficulty.

The small temperature-increase in the association of all vapours quoted is due to the great increase in the vapour density. This will be clear when the association formula is published.

The difference between my definition of temperature and that of Prof. Wilson is that I have identified temperature with energy, while Prof. Wilson defines a scale of temperature in which temperature appears as the product of pressure and volume divided by the gas constant, so that

$$T = \frac{pv}{R}.$$

Both definitions may lead to the same results, but my definition is the only one which can give a clear physical conception of the nature of temperature. The difference between the two definitions is illustrated by Prof. Wilson's doubt about the truth of my dimensional formula for temperature, which is an inevitable consequence of my definition.

As Dr Chatley remarks, my paper confirms Edser's views that the properties of matter are the result of molecular attraction, and that the force of attraction varies inversely as the eighth power of the distance. Edser deduced this law, and I have applied it to calculate the observed physical properties of gases and liquids. The law is supposed to hold up to the instant of collision. Actually it represents the average effect of attractions and repulsions, which depend on the orientation of the particles. When the solid condition is approached, and particles become more or less fixed in their positions, the question of orientation becomes important. Then the simple eighth-power law may not hold. It should not be impossible to devise a law that would take account of both attraction and repulsion, and thus to extend the discussion to the solid state.



Figure 1. Surface scum on mercury pipetted from glass.

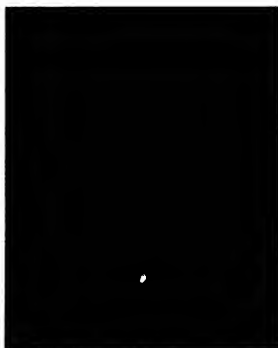


Figure 2. Thick surface skin on mercury.

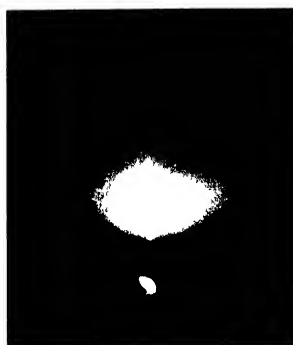


Figure 3. Thin surface skin on mercury.

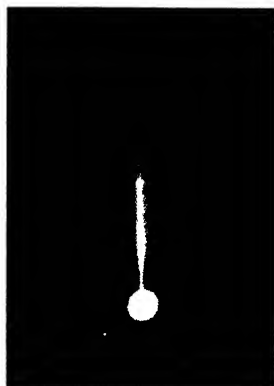


Figure 4. Surface skin of average thickness on mercury.



Figure 5. Gold evaporated on to a mercury surface skin.

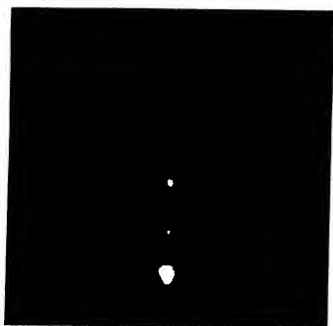


Figure 6. Gold amalgam formed on stirring.

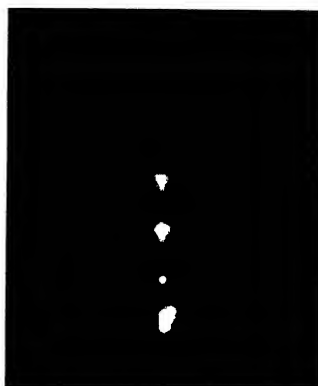


Figure 7. Mercuric bromide formed on a mercury surface.

THE SURFACE STRUCTURE OF LIQUID MERCURY

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ABSTRACT. Previous workers have obtained by electron-diffraction from liquid-mercury surfaces either evidence of a crystalline structure, which they attributed to the mercury, or inconclusive results in that only incoherent scattering was observed. The present work explains these discrepancies and shows that liquid-mercury surfaces are in reality amorphous, but are generally covered with a thin crystalline film of some adventitious impurity.

§ 1. INTRODUCTION

SEVERAL workers⁽¹⁾ have shown by X-ray diffraction that the interior of a mass of liquid mercury is amorphous. On the other hand Wierl⁽²⁾, Kakesita⁽³⁾ and Berdennikov, Bresler, Zelmanov and Schtrauf⁽⁴⁾ obtained by electron-diffraction evidence of a crystalline surface structure which led them to suggest that the surface of the liquid was crystalline, the structure being either face-centred-cubic⁽²⁾, face-centred-rhombohedral⁽³⁾ or hexagonal⁽⁴⁾. Trillat⁽⁵⁾, Raether⁽⁶⁾ and Papsdorf⁽⁷⁾, however, also using electron-diffraction, could find no signs either of sharp rings or even of haloes in their patterns obtained from liquid mercury at grazing incidence, and it is unlikely that this could have been due merely to a preponderance of inelastic scattering of the electrons. Trillat seems to have used a very small mercury drop, and the varying refractive effects due to the correspondingly large curvature of the surface may well have caused sufficient blurring to obliterate the diffraction pattern. Raether and Papsdorf used flowing, and therefore presumably exceptionally clean, mercury surfaces from which the metal should have been able to evaporate freely and unhindered by any surface skin of impurity. Experience has shown, however, that it is impossible to obtain satisfactory electron-diffraction photographs in a camera saturated with mercury vapour at room-temperature; thus, according to kinetic theory, at a pressure of 10^{-3} mm., 85 per cent of the electrons would collide with mercury atoms after diffraction in a camera with an effective length of 43 cm. Schöbitz⁽⁸⁾ has in fact stated that the pressure in his apparatus had to be less than 10^{-5} mm. before clear diffraction patterns could be obtained. Thus it would seem experimentally impracticable to record the electron-diffraction pattern from a clean mercury surface.

In the experiments described below, the main object of which was to study the structure of the liquid mercury surface, quiescent mercury pools alone were used. Repeated attempts were made to eliminate all traces of surface impurity, but these were never entirely successful although in some cases the scum thickness was

reduced to such an extent as to permit penetration by the electron beam down to the underlying mercury surface. Thin though such a skin must have been, it evidently sufficed greatly, if not indeed completely, to suppress the evaporation of mercury, because otherwise it is difficult to see how clear diffraction patterns could have been obtained.

§ 2. EXPERIMENTAL

The electron-diffraction camera used was similar to that described by Finch, Quarrell and Wilman⁽⁹⁾ but was built for use in a horizontal position. The camera length was 43 cm., and the accelerating potential usually about 50 kv. The mercury was contained in an ebonite or iron cup, 3 cm. in diameter, filled brim-full, and previously cleaned with redistilled benzene. When the ebonite cup was used the mercury was earthed by means of a fine platinum wire. The nature of the container had no effect upon the results obtained.

The mercury was cleaned by repeated washing in 10-per-cent nitric acid solution and distillation in air at a few centimetres pressure, and gave a surface with an untarnished appearance. Nevertheless, after filtration into the cup through a dry filter-paper pierced with a small hole, or after transference by means of a clean glass pipette, a pattern, figure 1, was obtained consisting of short arcs and evidently due to an oriented surface impurity, since the spacings deduced from the pattern bore no relation to the known structure of mercury. The next surfaces were therefore prepared by sucking over into the apparatus under high vacuum, the mercury being withdrawn from well below its surface in an external vessel in order to leave behind the surface film. The patterns obtained from such surfaces varied from a series of sharp spots normal to the edge of the shadow of the specimen, figure 2, through all stages of resolution to a faint continuous streak corresponding to a film thickness of only a few layers of atoms, figure 3. When the streak was faint and practically continuous and the surface film therefore extremely thin, two faint haloes also were obtained, and these were undoubtedly due to the underlying mercury surface. Thus the halo-diameters agreed sufficiently well with those obtained by X rays from liquid mercury. For example, the second halo, which was the most suitable for measurement, gave a spacing of 1.3 ± 0.1 Å. as compared with 1.4 Å. obtained by X rays. It was not found possible to determine the nature of the adventitious polycrystalline surface film. The pattern was similar to a rotation photograph, and an orthorhombic structure could be assigned in which $a = 3.40$ Å., $b = 3.92$ Å., and $c = 6.8$ Å., the (100) planes being parallel to the surface. This does not agree with the known structure of mercuric oxide, nor did the film thicken on exposure to air; hence it seems that the film could not have been caused by surface oxidation. The spots observed by Raether⁽⁶⁾ were probably due to the same substance, since the observed spacings are identical. The relative intensity of the halo pattern could be increased to a limited extent by heating the surface *in vacuo* by radiation from a white-hot tungsten filament.

The mercury surfaces used in the next experiments were covered with a surface film of such thinness that the row of spots normal to the shadow-edge was drawn

out by refraction and lack of resolution into a continuous streak of varying width, figure 4. The effective length of the crystals normal to the mercury surface may be estimated as follows. With very thin crystals, the inner potential causes electrons that have been diffracted by true reflection to strike the photographic plate not at the region of normal maximum intensity, but somewhat nearer to the central spot. The Scherrer type of equation may, however, be applied to those parts of the diffraction which lie on the sides of the intensity maxima away from the undeflected beam, since these can be produced only by electrons which are diffracted by transmission. In this way the average thickness of the films on the mercury surfaces was estimated as 9 Å. We have verified Scherrer's equation with patterns obtained from unimolecular films of hydrocarbons of known chain length; thus with a monolayer of dotriacontane, $C_{32}H_{66}$, which has a chain-length of 39 Å., the half-width of the layer lines not deflected by inner potential gave a calculated length of 37 Å. Similar film-thickness measurements with monolayers of other hydrocarbons down to $C_{22}H_{46}$ also gave results which sufficed to show that Scherrer's equation can be relied upon as a first approximation in the special case under consideration.

The wide differences in the patterns obtained from the surfaces of mercury render it unlikely that they were due to any surface crystallinity of the mercury itself. In order to obtain definite information on this point, films of readily amalgamated metals were evaporated on to such surfaces. Immediately after condensation from the vapour on to a still mercury surface, a pattern, figure 5, characteristic of gold in pronounced (111) orientation was obtained, and provided that any disturbance of the mercury surface was avoided the gold pattern remained unchanged, showing that the surface skin of unknown material acted as an effective barrier between the gold and the mercury and, indeed, must also have been effective in preventing escape of mercury vapour. After stirring with a glass rod, however, the gold pattern gave place to one characteristic of a face-centred-cubic structure in which $a = 5.58$ Å., figure 6. This structure differs from those of the gold amalgams previously studied by Aylmer, Finch and Fordham⁽¹⁰⁾. Silver on evaporation gave initially a pattern of arcs due to a substance of unknown structure; when the surface was left standing, the arcs merely tended to lengthen into rings, but after agitation of the surface a pattern similar to that of the gold amalgam was obtained. Evaporated aluminium gave initially two haloes, but after the surface had been kept standing in air, a sharp ring pattern was obtained corresponding to a face-centred-cubic structure of side 3.74 Å.; this does not correspond to any known structure of aluminium or of its oxide or hydroxides. Cobalt and chromium also gave very diffuse rings, but in these cases no change occurred on standing or agitation.

Further confirmation of the view that the arc and spot patterns were due to a surface impurity was obtained by the study of the action of ozone. This is known to oxidize agitated and therefore clean mercury surfaces to a slight extent at room-temperatures, although no visible reaction occurs with stationary surfaces. In our experiments, ozone at a concentration which amply sufficed to cause mercury to tail on glass or to blacken heated silver merely produced a slight reduction in the intensity of the initial streak, the halo pattern remaining unchanged. Therefore,

apart from the unlikely event of the formation of a very thin protective film of an amorphous oxide, it must be concluded that the surface film, although only a few atom layers thick, afforded virtually complete protection of the mercury beneath from attack by the ozone.

The surface film could be broken by more energetic reagents, such as the halogens. These then attacked the mercury surface to form the orthorhombic mercuric halides in (010) orientation, the pattern, figure 7, of mercuric bromide being typical of those obtained in this manner; the *b* axis is here taken as that with a spacing intermediate between the shorter *a* and longer *c* axes. The iodide film was therefore probably the yellow mercuric iodide, but this could not be verified visually since the films were so thin as to show only first-order interference colours. In all the patterns the central row of spots was extended by refraction and lack of resolution to form a streak similar to that observed with the mercury surfaces themselves; the spacing of the spots was, however, characteristic of the halides and not of the surface impurity.

§ 3. DISCUSSION OF RESULTS

The photographs obtained from liquid-mercury surfaces may be resolved into two constituent diffraction diagrams. One, characteristic of a crystalline compound, must be due to a surface impurity for the following reasons. First, the diagram obtained varied from an arc pattern, when no great care was taken to obtain a very clean surface, to a streak normal to the plane of the liquid surface when special precautions aiming at the formation of a skin-free surface had been taken. Such a streak is characteristic of a very thin continuous film examined by reflection; similar diagrams can be obtained, for example, from slightly oxidized or corroded copper surfaces. Secondly, entirely different crystal structures have been obtained in the present work and by each of the three previous investigators, a fact which can be reasonably explained only by assuming the presence of an adventitious surface scum. Thirdly, ozone was found to have no effect on the mercury. Finally, experimental proof of the existence of the skin is afforded by the fact that gold evaporated on to the mercury surfaces was not attacked unless the mercury was agitated. This experiment is of particular interest in connexion with the work of Finch, Quarrell and Roebuck⁽¹¹⁾, who showed that the Beilby layer on certain polished metals is capable of dissolving other metals to a remarkable extent provided that the polished surface is free from a contaminating film of grease or oxide.

The second type of diffraction pattern, consisting of two haloes, was observed only when the surface film was extremely thin (less than about 10 Å.) and was therefore due to the underlying mercury surface. This interpretation is supported by the fact that the halo-diameters were those to be expected from liquid mercury. The conclusion must therefore be drawn that, in contradiction to previous statements, the surface of liquid mercury is truly amorphous and has the same structure as that obtained for the interior by means of X-ray diffraction. As a general rule, however, a mercury surface is covered with a more or less thin crystalline skin of some adventitious impurity, even though special precautions may have been taken to prevent such a film from forming.

§ 4. ACKNOWLEDGEMENTS

The authors thank Professor G. I. Finch for his unfailing interest and advice, and one of them (S. F.) wishes to thank the Department of Scientific and Industrial Research for a grant.

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DISCUSSION

Dr R. O. JENKINS: I have read this paper with interest, as it repeats results I obtained over three years ago, which may be found in my London University Ph.D. thesis. In my experiments I found that ordinary clean mercury gave a pattern similar to that in figure 3, consisting of the line which I attributed to a thin oriented oxide layer, and two diffuse haloes from the underlying mercury. By drawing freshly distilled mercury under vacuum into the apparatus and then using it to overflow the surface, it was found possible almost to eliminate the surface skin line, leaving only the haloes from the mercury itself. Their lattice spacings were 2.47 and 1.33 Å. respectively, while X-ray work indicates values of 2.56 and 1.39 Å. The slight discrepancy is possibly due to atoms being more closely packed near the surface as a result of the atomic forces on them being asymmetrical, the net effect being to pull the surface atoms into the liquid.

The authors have however made an important omission in failing to discuss the possibility of refraction in their interpretation of the two diffuse haloes. If the surface is electron-optically flat, the haloes will be displaced from their true positions. It can be shown that if the inner potential has the likely value of about 15 v., the second halo when refracted will be where the first one was, and a possible third halo will take the place of the second to within close limits. Owing to the diffuseness of the haloes, this effect would not be observed. It is possible however by varying the angle of incidence of the electron beam on the mercury surface to alter the

radius of the outer halo by about 12 per cent if it is a refracted halo. This change however could not be detected in practice, and it seems probable that the haloes were not refracted and that the mercury surface was therefore not electron-optically flat.

Dr H. CHATLEY: Will the authors define "amorphous"?

Dr O. KANTOROWICZ: As to the meaning of the terms amorphous and crystalline, I would like to draw attention to a paper by B. E. Warren in the October issue (1937) of the *Journal of applied Physics*, in which he discusses this problem in respect of fused silica. He states that if one tentatively assumes fused silica to be composed of minute crystals of cristobalite and estimates their size by Bragg's formula from the broadening of Debye-Scherrer rings, the average size of the assumed crystals is found to be 7.7 Å. On the other hand the length of a unit cell of cristobalite is 7.0 Å. It follows that the assumed crystals on the average do not contain more than one unit cell, and that there is no indication of an extended lattice. Dr Warren concludes that there is no sense in debating whether fused silica is amorphous or composed of small crystals, for these crystals, if they exist, must be so small that the arrangement of atoms would not be different from that in an amorphous mass. I entirely agree.

The authors say that no difference can be established by their method if their crystal-size is as small as 15 Å. That is not surprising. Let us assume an even bigger crystal of cubic form and containing 1000 atoms. One realizes at once that of these, 488 are situated on the very surface of the crystal. That means that for about half the atoms the distances to about 20 per cent of their nearest neighbours (e.g. those in the neighbouring crystal) are not determined by the laws that govern the regular spacing inside the crystal. Consequently all methods that are based on the interference of wave trains originating from evenly spaced atoms will give disturbed results, the degree of disturbance increasing with decrease in particle-size as more and more atoms find themselves on the surface. (For instance the disturbance is 80 per cent for 5^3 or 125 atoms.)

As the sensitivity of different experimental methods as to the misarrangement of atoms might be different, one and the same body might with one method indicate an amorphous, random distribution of atoms, and with another method a crystalline lattice. On the other hand, for each method there will be a maximum particle-size below which the distinction between crystalline and amorphous states becomes inapplicable in principle. In this range any discussion as to the state of the body must be fruitless. I therefore submit the terms "amorphous" and "crystalline" should be used in relation to the method of investigation only.

Reply by Dr FORDHAM: I am interested to hear that Dr Jenkins has obtained experimental results similar to ours, although as a result of our experience, and not having seen Dr Jenkins's photographs, I am still somewhat dubious as to the possibility of obtaining satisfactory electron-diffraction photographs from a perfectly clean mercury surface. Like Dr Jenkins, we could find no evidence of refraction and therefore did not discuss its possible effects. A similar lack of refraction has

been noted by French in the case of the Beilby layer. Owing to the large angles of incidence employed in our experiments, the maximum change introduced in the diameter of the second halo by an inner potential of 15 v. would only have been about 10 per cent. Such refraction would have caused appreciable lack of circularity about the central spot, but no such eccentricity was ever observed. These considerations, of course, have little or no bearing on the determination of the structure of the liquid mercury surface, although they may indicate, as Dr Jenkins suggests, that liquid mercury surfaces are not electron-optically flat.

In reply to Dr Chatley; I should call "crystalline" any substance in which the constituent atoms are arranged regularly for at least two unit translations in all directions, and also larger two-dimensional networks. All other substances I should call "amorphous". The difficulty of definition arises from the fact that the terms "amorphous" and "crystalline" are not mutually exclusive, but refer merely to two extreme types of large-scale structures.

Thus, whilst agreeing in the main with the remarks of Dr Kantorowicz, I prefer a definition of "amorphous" which is independent of experimental method and which embodies only the general conception of crystallinity as regular repetition in all directions. Dr Kantorowicz seems to overestimate the importance of inter-crystalline scattering; the nature of the interference function is really such that even with a bimolecular liquid the positions of the maxima are determined largely by the intermolecular spacing. Since, however, crystalline spacings are in general not very different from the closest distance of approach of atoms in the corresponding monatomic liquid, it cannot be said that the X-ray or electron-diffraction results rule out the possibility of a small degree of association in liquid mercury, but our results do show that the surface has fundamentally the same structure as the interior of the liquid, and that the large-scale crystallinity reported by previous workers was due to films of impurity.

VIBRATIONS OF FREE CIRCULAR PLATES.

PART I: NORMAL MODES

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ABSTRACT. The normal vibrating modes of free circular plates have been determined over an interval of more than six octaves, the solid-carbon-dioxide method of excitation being used to produce the nodal figures, and a valve oscillator to measure their frequencies. It is concluded that the nodal system of ideally uniform and entirely free plates would, in accordance with theory, consist only of circles, diameters and combinations of circles and diameters. It is found that although each simple mode has its characteristic frequency, cases occur in which the difference between two or even three of these is very small, and the number of nodal diameters, which as regards raising the pitch are approximately equivalent to one nodal circle, increases from two to five, in the interval investigated, in passing from figures with relatively more circles to those with relatively more diameters. The expression, based on approximate theory, for calculating the frequencies of the higher modes, in which it is assumed that the addition of two nodal diameters increases the frequency by as much as one nodal circle, is accordingly not applicable in ordinary practice.

It is suggested that the simple and rapid solid-carbon-dioxide method of exciting free vibrations might be employed for testing the uniformity of plates, for detecting internal flaws, for studying recrystallization phenomena, and for obtaining comparative values of Poisson's ratio of metals and alloys.

§ 1. INTRODUCTION

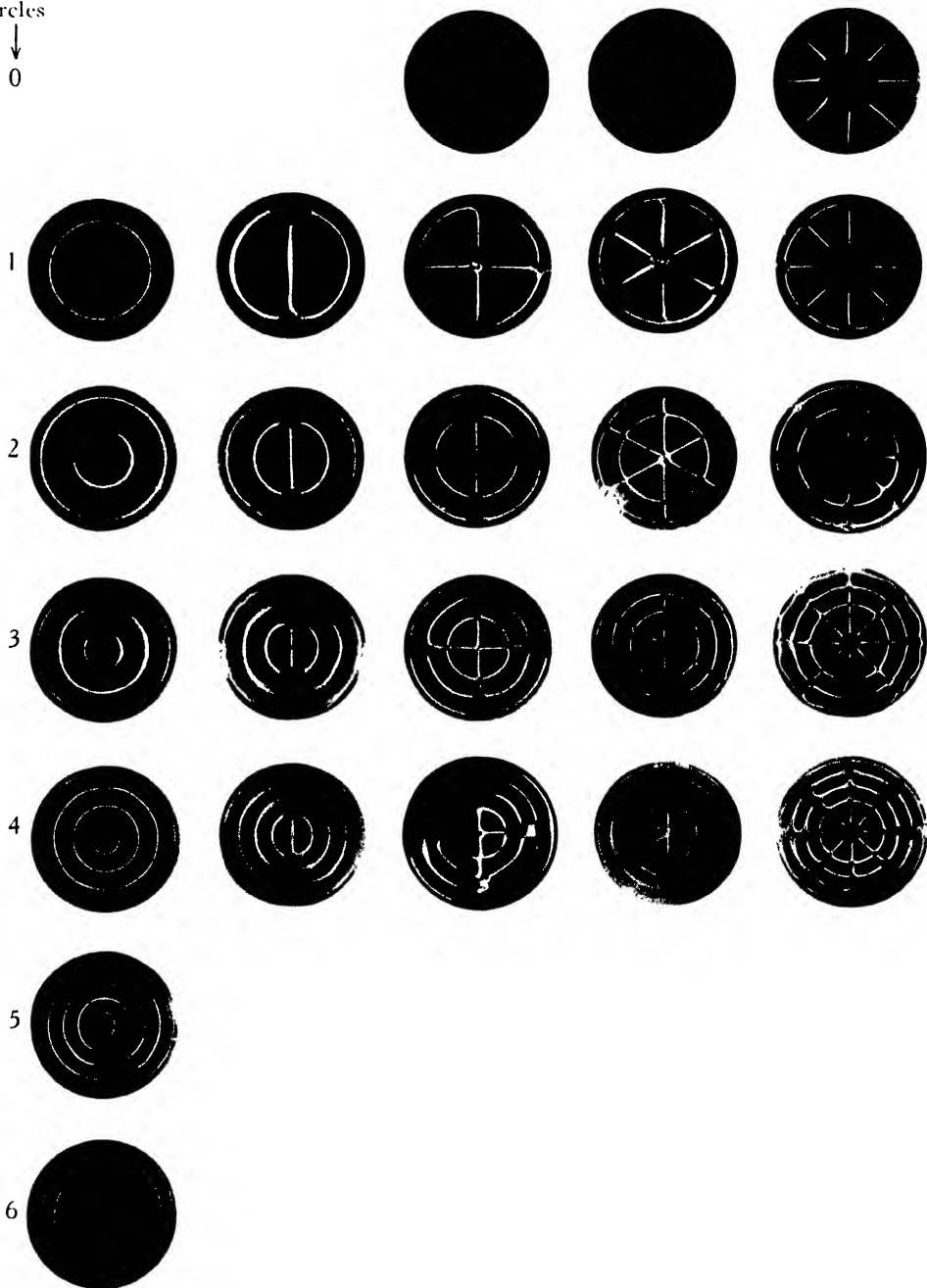
THE main facts regarding the vibrations of free circular plates, both theoretical and practical, are given in Rayleigh's treatise on *Sound*, vol. 1, chapter 10 (§§ 218–23). The critical discussions and suggestions made not only in this chapter, but also in the preceding one which deals with vibrating membranes, have been much used in connexion with the present work.

The nodal figures of free circular plates, as also those of any other system of revolution, should, according to theory, consist of diameters symmetrically distributed round the centre, but otherwise arbitrary, together with concentric circles. In practice, however, it is well known that many other designs are frequently produced, which have never been systematically studied or adequately explained. The solid-carbon-dioxide method of producing vibrations⁽¹⁾ possesses peculiar advantages for doing this since vibration frequencies other than those natural to the plate cannot be produced and the excitation can be made on any part of the surface. It appears that the most extensive list of observed normal vibration frequencies of free circular plates is still that of Chladni⁽²⁾. His results are given in the notation of the chromatic scale, and in view of the apparatus at his disposal they are necessarily

Diameters $\rightarrow 0$

Circles

\downarrow
0



Normal vibrating modes of free circular plate.

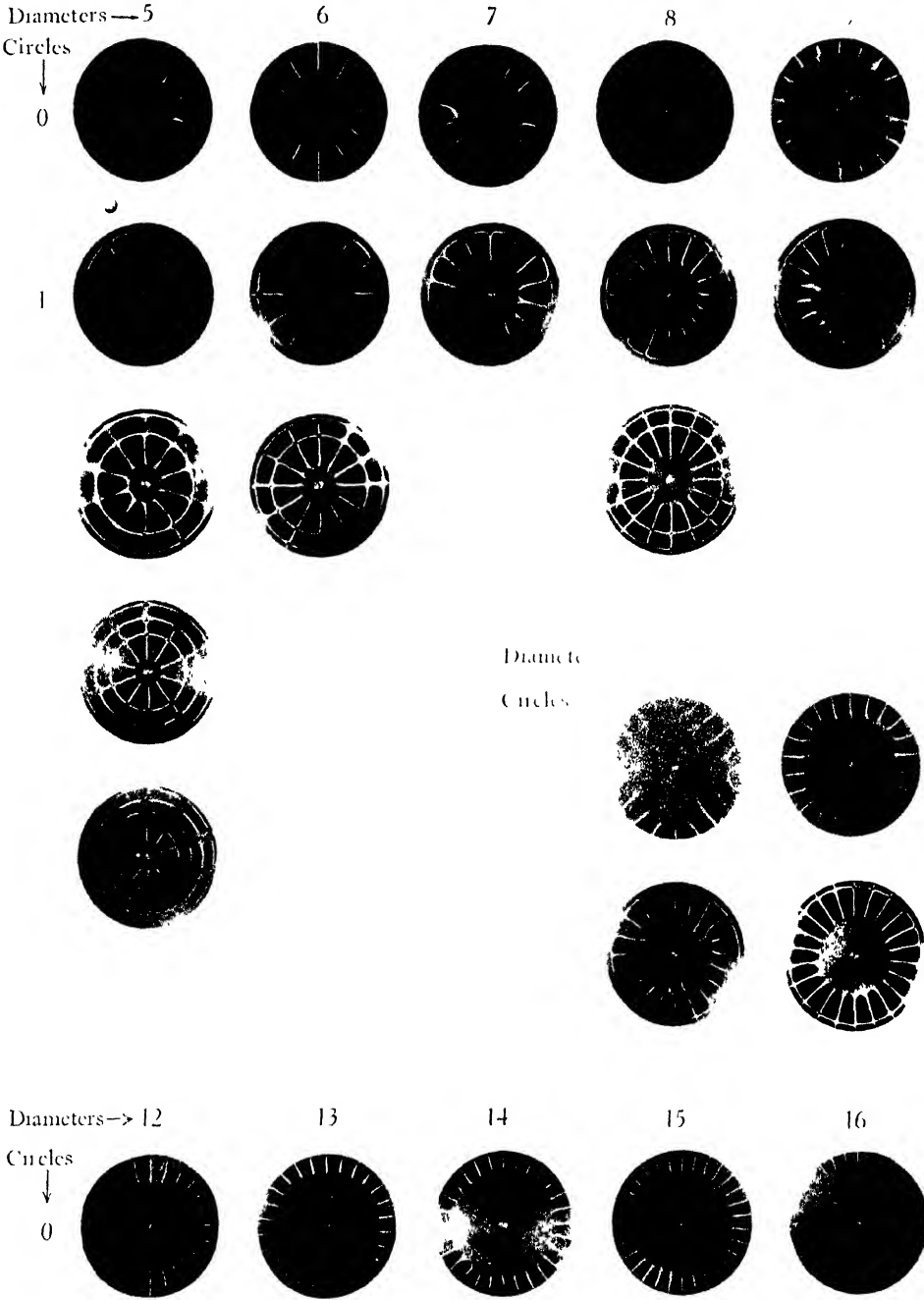


Plate 2. Normal vibrating modes of free circular plate (*cont.*).

only approximate. They do not extend far enough to explain the greater number of his own nodal patterns nor those produced during the present investigation. Strehlke's⁽³⁾ measurements of the radii of nodal circles will be referred to in due course.

Kirchhoff's theoretical frequencies, which on account of the lengthy calculations involved are restricted to the graver tones, will be considered later, and it will then be shown that the approximate expression for calculating the higher partials is not generally applicable in practice.

The present part of the paper describes and discusses the observations that have been made to obtain the frequencies and nodal systems of the normal vibrating modes over an interval of about six octaves. Part 2 will be concerned with a large number of nodal designs, other than those consisting of circles and diameters. As a result of these studies it has been found possible to interpret Chladni's original figures on circular plates, and these are considered in part 3.

§ 2. EXPERIMENTAL ARRANGEMENTS

Frequencies. The frequencies of the vibrations were determined by the method of beats by means of a mains operated calibrated valve oscillator.

Plates. A considerable number of plates of different sizes were employed, but final measurements were restricted as far as possible to large and thin plates. The diameters of two of these, for example, were 30.47 and 25.71 cm. respectively, the thickness in each case being approximately 2 mm. The importance of using thin plates is emphasized by some recent work of A. B. Wood⁽⁴⁾ in which he shows how the frequencies of the two gravest tones of free circular plates gradually diminish as the ratio of thickness to diameter increases.

Supports and manner of excitation. When figures with a central node were obtained, the plates were supported centrally in the usual manner. The diameter of the hole in the plate was 5 mm. In order to obtain the nodal circles, the plate under test (preferably one without a central hole) was laid on three equidistant small circular-sectioned pieces of indiarubber, which were placed in appropriate nodal positions on a horizontal table provided with a paper scale graduated in circles and angles. With the first arrangement of support, the solid carbon dioxide was usually applied to the under surface of the plate, and with the second arrangement to the upper surface. A second translucent graduated scale, which could be laid on the surface of the plate, was often found useful in deciding on the point of excitation. While the surface was being sprinkled with sand this position was protected by means of a small proof plane which was afterwards removed. A desired nodal figure was also sometimes encouraged by gently touching the plate at one or two appropriate nodal positions by means of a divider. In order to obtain the best figures the experiments were made on dry days⁽¹⁾, dried sand being sprinkled just before the excitation on polished plates from which any grease had been removed with xylol. The Drikold solid carbon dioxide used for exciting the plates was very kindly given by Imperial Chemical Industries Ltd.

Photographs. Since it was desirable, for purposes of comparison, that all nodal figures should be given on the same scale, some of the photographs shown in the

plates are enlargements of the original photographs. The two to eight diameter-only figures, obtained in the first instance on small vibrating plates by means of solid carbon dioxide, have been replaced by figures produced by bowing on the larger vibrating plates.

Radii of nodal circles. The radii of the nodal circles were measured directly on the vibrating plates and the results confirmed subsequently on the photographs, either a travelling microscope or a projection lantern being used.

§ 3. EXPERIMENTAL RESULTS

The nodal systems extending over an interval of nearly six octaves are shown in plates 1 and 2, in which each column contains figures with a given number of nodal diameters and each row figures with a constant number of nodal circles. In most of the figures, the small want of uniformity in thickness which is generally present in large metal plates cannot be detected, but in the symmetrical figures of the first column a variation in thickness which was found to be less than 1 per cent has been sufficient to cause a considerable distortion in the innermost circles of the 4/0, 5/0 and 6/0 figures. The longer diameter corresponds with the direction of smaller thickness. At the 0/10 figure there is a very significant break in the regularity of the diameter figures of the first row. It was subsequently found possible to obtain figures without this irregularity on some particularly uniform steel plates kindly lent to me by Professor Andrade.

For the frequencies of the vibrations the various nodal systems are expressed as multiples of the gravest, 0/2 mode (i.e. the mode characterized by 0 circles and 2 diameters), and are given in table 1. It will be seen that although each frequency is

Table 1. Relative frequencies of normal vibrating modes of free circular brass plate

Diameters Circles													
	0	1	2	3	4	5	6	7	8	9	10	11	12
0			1*	2.29	4.10	6.19	8.80	11.7	15.1	18.8	23.0	27.6	33.0
1	1.70	3.99	6.79	10.3	13.8	18.1	23.1	28.6	34.7	40.8	47.5	54.7	63.0
2	7.51	11.7	16.1	21.2	27.1	33.4	40.5	47.7	56.0	65	75	86	100
3	16.4	22.7	29.4	36.3	43.0	50.5	59	69	80	90	(104)	(118)	(135)
4	29.1	37.0	43.2	53.1	63.0	74	86	99	(120)	(145)			
5	47.0	56.0	66	77	92	(110)	(135)						
6	72.7	83	100	(127)	(147)								
7	(110)	(132)	(160)										
Diameters Circles													
	13	14	15	16	17	18	19	20	21	22	23	24	
0	38.0	44.5	51.0	58.0	65.5	74.3	83.5	90.9	100	109	118	127	
1	72.5	(81)	(90)	(97)	(108)	(120)	(135)						
2	(115)												

The figures in italics are approximate and those in brackets have been estimated by extrapolation only or by rough measurements on a large plate 46.7 cm. in diameter.

* Actual frequencies of the plates 30.47 and 25.7 cm. in diameter were 80.9 and 113.3 c./sec. respectively.

distinct, cases occur in which there is very little difference between two or even three of the numbers. In particular the 0/10 relative frequency, 23.0, is very near to that of the 1/6 mode, 23.1. It becomes evident, then, that the imperfect 0/10 nodal figure is due to the double circumstance of a departure from perfect symmetry in the plate and a near coincidence of natural periods. We shall return to this important result in part 2. Other small irregularities will also then receive an adequate explanation.

Table 1 also includes some further frequencies which have been obtained either by extrapolation or from recent observations which have been made without photographing the nodal systems. Some of the approximate numbers of the highest partials are in *italics*; they will be needed in parts 2 and 3. Measurements of the radii of the nodal circles, given relatively to the plate's radius, are shown in table 2.

Table 2. Radii of nodal circles relative to that of the disc, taken as 1000

Diameters Circles	0	1	2	3	4	5	6	7	8	9	10	11
1	680	781	823	843	859	871	880	889	897	903	909	912
2	391	497	562	604	635	662	681	702	715			
	843	867	887	898	906	915	922	927	932			
3	257	349	415	461	505	531						
	591	643	681	706	728	745						
	895	902	913	919	925	933						
4	190	269	328	374	411	443						
	441	495	540	571	596	623						
	692	726	748	764	779	794						
	918	928	934	938	941	944						
5	154											
	351											
	548											
	753											
	956											
6	131											
	292											
	456											
	624											
	794											
	958											

§ 4. COMPARISON WITH PREVIOUS RESULTS AND WITH THEORY

Chladni's law. It is evident from table 1 (see also the last column of table 1, part 2) that Chladni's experimental conclusion⁽²⁾, which states that the addition of 2 nodal diameters raises the pitch by approximately the same amount as that of 1 nodal circle, has not been substantiated. This number increases from 2 to 5 in the interval investigated, being least for the vibrating modes shown on the lower left-hand side and greatest for those shown on the upper right-hand side of the table. Since the approximate expression (see below) for calculating the frequencies of higher partials also makes the assumption made by Chladni, it has been necessary to examine the evidence very carefully.

A study of Chladni's work^(a) shows that he was more interested in producing nodal circles than in producing nodal diameters, and that whenever possible he supported and controlled his plates by hand. His table of frequencies extends only to 8 nodal diameters, but as far as 6 nodal circles which characterize roughly the same pitch as 18 diameters. It appears that he must have formulated his law with reference to the frequencies at the lower left hand of table 1 of the present paper. This is all the more curious since his own table gives evidence of three diameters being equivalent to one circle. For example the pitch g' is given both for figure 0/5 and for 1/2, b'' for 0/8 and 2/2, and g''' for 1/7 and 2/4. His nodal figures, which are the subject of part 3, also provide much evidence of more than two diameters being equivalent to one circle.

According to the approximate expression⁽³⁾ for calculating the higher roots of Kirchhoff's free-plate equation the frequencies of the normal vibrating modes are proportional to $(n + 2h)^2$, where n is the number of diameters and h is an integer. It will be best to quote Rayleigh's own words, in which the expression in question is quoted as (4)*: "It appears by a numerical comparison that h is identical with the number of circular nodes. . . . *Within the limits of application of (4), we see also that the pitch is approximately unaltered, when any number is subtracted from h , provided twice that number be added to n . This law, of which traces appear in the following table, may be expressed by saying that towards raising the pitch nodal circles have twice the effect of nodal diameters. It is probable that, strictly speaking, no two components have exactly the same pitch.*"

It appears from the present observations, that Chladni's law applies to very few of the partials in the first six octaves. When it is remembered that Kirchhoff's theory was formulated for thin plates and how the nodal diameters crowd up to the centre of the plate it is scarcely to be expected that any constant relation will exist between the number of nodal diameters and nodal circles which must be added in order to raise the vibration frequency by the same amount.

Before leaving this subject it is interesting to note that A. B. Wood⁽⁴⁾ found a tendency for his 1/0 observations to yield somewhat higher values of velocity of sound than those derived from 0/1 observations.

Poisson's ratio. In the case of transversely vibrating plates, both Poisson's ratio and Young's modulus are factors determining the frequency of vibration, which, other conditions being constant, should vary with the material of the plate.

Since Chladni preferred glass to metal plates, it may fairly be assumed that his observations correspond to a value of Poisson's ratio σ such that $\sigma \doteq \frac{1}{4}$. A few vibration frequencies obtained with plates made of brass, for which $\sigma \doteq \frac{1}{3}$, and steel, for which $\sigma \doteq \frac{1}{4}$, are compared with Chladni's results in table 3, in which also some calculated frequencies due to Kirchhoff⁽³⁾ for values $\frac{1}{3}$ and $\frac{1}{4}$ of σ are included.

It will be seen that an alteration of σ from 1/4 to 1/3 produces nearly a 7 per cent increase in the relative frequency of the 1/1 mode. These results are sufficiently striking to make further observations on plates of identical dimensions but of varying

* The italics are mine, and the table to which he refers extends only as far as 2 circles and 3 diameters.

Table 3. Comparison of results. Frequencies relative to that of the gravest mode, 0/2

Circles	Diameters	Material of plate. Observed relative frequencies			Kirchhoff's calculation ⁽³⁾	
		Brass $\sigma = \frac{1}{3}$	Steel $\sigma = \frac{1}{4}$	Chladni glass* $\sigma = \frac{1}{4}$	$\sigma = \frac{1}{3}$	$\sigma = \frac{1}{4}$
1	0	1.7	—	1.60	1.73	1.61
1	1	3.99	3.77 3.82	3.75	3.91	3.70
0	4	4.10	4.12 4.03	4.0	4.05	—

* The measurements were almost certainly made on glass plates⁽²⁾.

material desirable. Table 4 may also be examined in connexion with this subject. In it Strehle's⁽³⁾ measurements on glass plates have been compared with the present measurements made on brass plates and with Kirchhoff's calculated values for $\sigma = \frac{1}{3}$ and $\frac{1}{4}$ respectively. It is perhaps just possible to detect the influence of Poisson's ratio in the later figures.

Table 4. Comparison of results. Radii of circular nodes (radius of disc = 1000)

Circles	Diameters	Observed on brass $\sigma = \frac{1}{3}$	Strehle Observed on glass $\sigma = \frac{1}{4}$	From Kirchhoff's theory	
				$\sigma = \frac{1}{3}$	$\sigma = \frac{1}{4}$
1	0	680	678	—	681
2	0	391	391	—	391
		843	841	—	842
3	0	257	256	—	257
		591	591	—	591
		895	894	—	894
1	1	781	782	780.8	781.4
1	2	823	810	822.7	821.9
1	3	843	840	846.8	845.2
2	1	497	490	497.1	497.7
		867	869	870.1	870.6

Measurements made on Chladni's drawings are not included since the results are variable.

§ 5. CONCLUSIONS

(1) By means of the solid-carbon-dioxide method of producing vibrations in metal objects it has been possible to obtain all the normal vibrating modes of free circular plates which occur in an interval of over six octaves.

(2) The nodal system of ideally uniform and perfectly free circular plates would consist, in agreement with theory, only of circles, diameters, or combinations of circles and diameters.

(3) The vibration frequencies of the normal vibrating modes are all distinct. Occasionally the frequencies of two or even three modes are very nearly equal.

(4) The number of nodal diameters which must be added to raise the frequency by as much as one nodal circle is not constant, but increases from two to five in the interval investigated. This increase occurs in passing from figures with relatively more circles to those with relatively more diameters. Approximate expressions for calculating the higher partials, which assume that this number is always equal to two, are accordingly inapplicable in practice.

(5) The relative frequencies of the overtones are appreciably affected by the value of Poisson's ratio in a manner which is in general agreement with theory.

§ 6. SUGGESTED APPLICATIONS

The following are some possible future applications of the solid-carbon-dioxide method of producing vibrations:

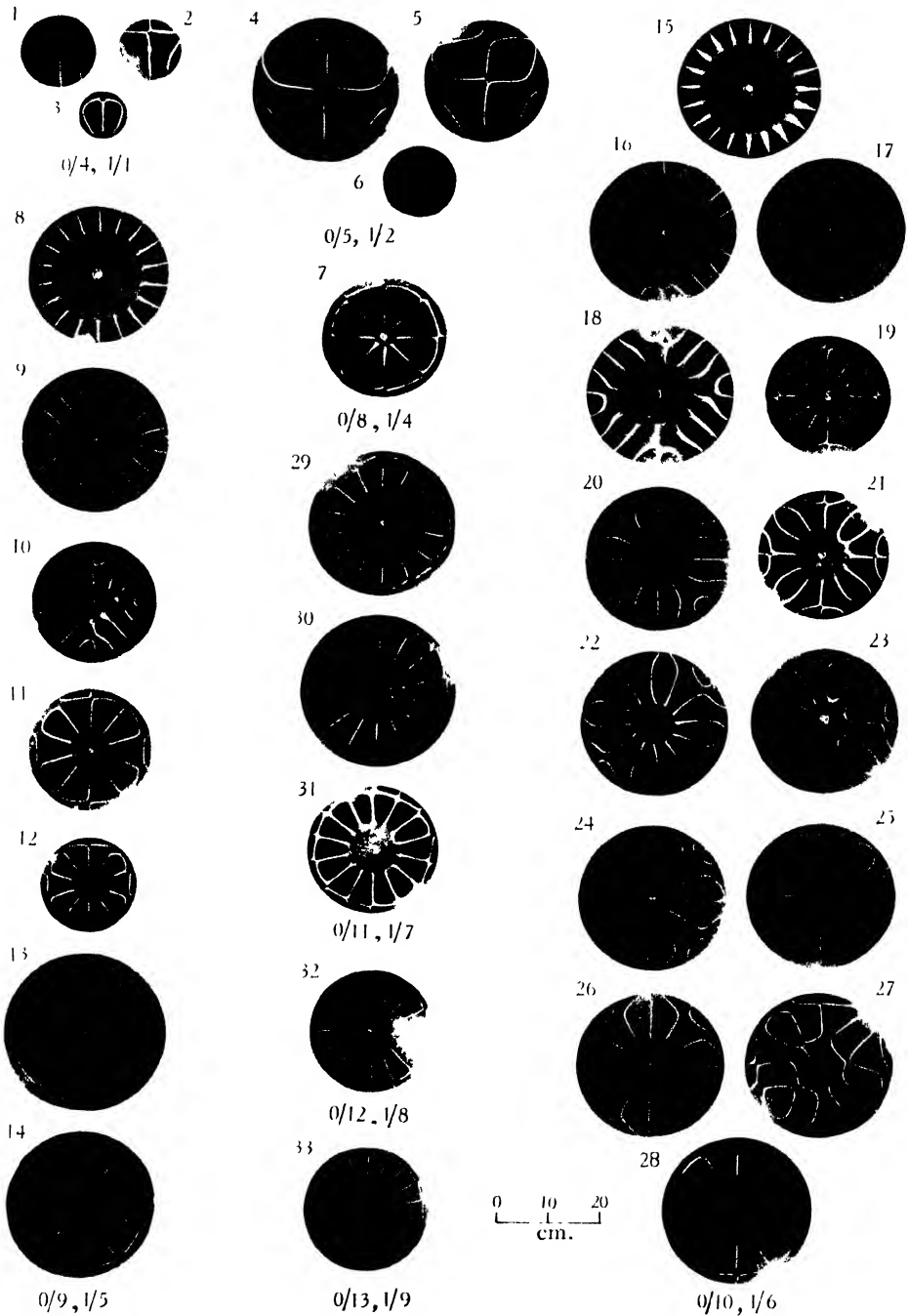
(1) *Rapid tests of uniformity of metal plates and detection of flaws.* Any departure from symmetry of a circular plate is at once apparent in the innermost nodal circle of the symmetrical nodal figures and this provides a sensitive method of detecting want of uniformity in plates. In this connexion it may be mentioned that a magnetostriction oscillator has recently been employed by Hayes⁽⁵⁾ for the detection and location of laminations in steel plates.

(2) *Study of recrystallization phenomena.* It would be interesting to study alterations in the nodal figures, more especially perhaps in nodal circles, which would occur when a metal plate which had been rolled in one direction only was heated until recrystallization occurred. This subject has already been studied by Tammann and his collaborators^(6,7) principally on the two-diameter and three-diameter nodal figures produced by bowing.

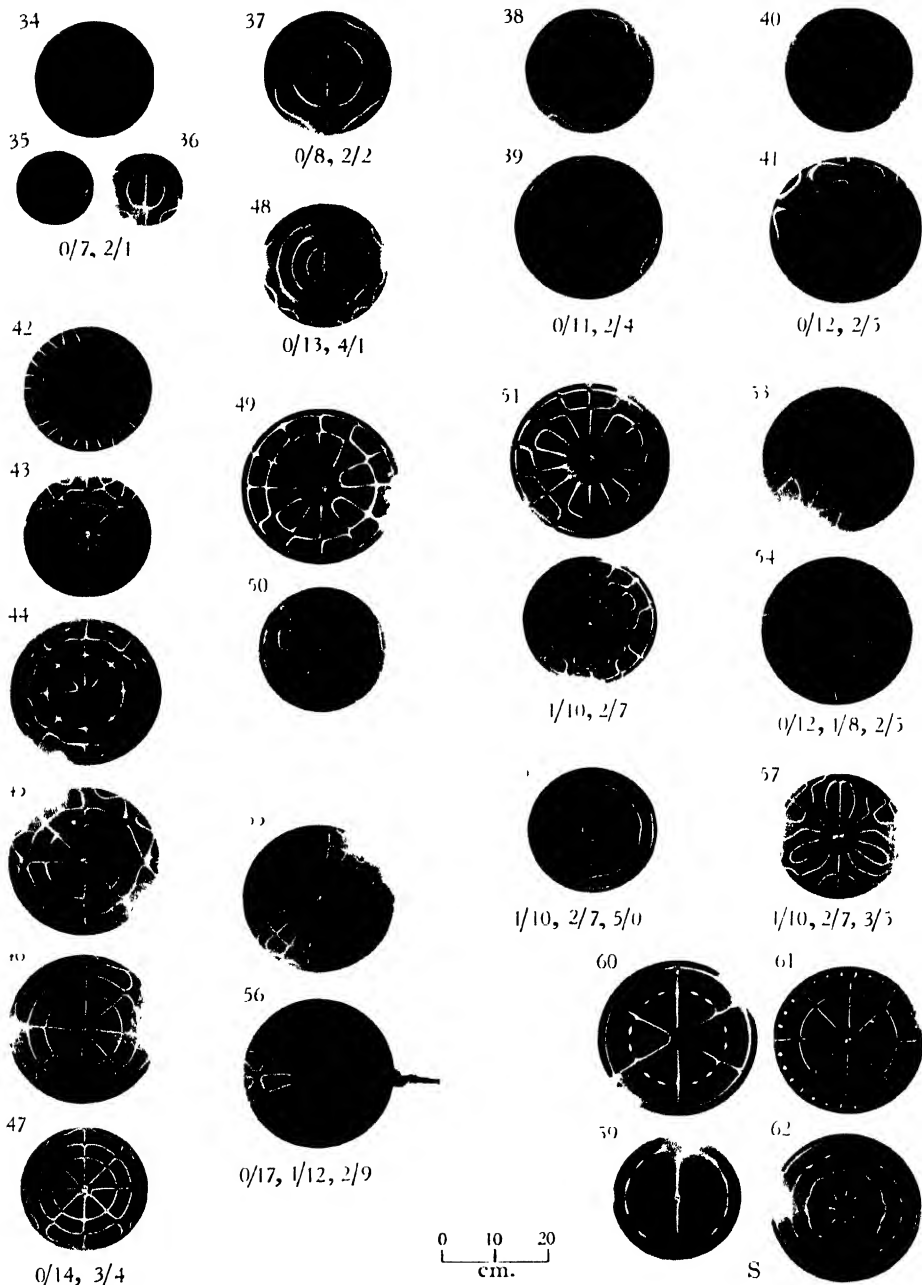
(3) *Comparative measurements of Poisson's ratio of metals and alloys.* It has been shown in table 3 that an alteration in the value of Poisson's ratio has an appreciable effect on the relative frequencies of the normal vibrating modes, which is possibly sufficient to provide a simple means of obtaining comparative values of Poisson's ratio for different metals.

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Combination of two vibrating modes.



Compounded normal modes of vibration.

VIBRATIONS OF FREE CIRCULAR PLATES. PART 2: COMPOUNDED NORMAL MODES

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ABSTRACT. The many nodal designs (other than those consisting solely of circles and diameters) which are obtained on free circular plates are shown to consist of two or more compounded normal modes of vibration, the periods of which are very nearly equal. The vibration frequencies corresponding to the designs are intermediate between those of the combining modes. The figures are produced as a result of the slight divergence of free periods which exists in all but ideally uniform plates. An increase in damping, either internal or arising from the manner of support or of excitation, also favours the production of these designs, since it renders the resonance less sharp. Compounded modes of a somewhat similar character may be expected to occur in other systems of revolution, such as circular plates clamped at the edge, circular membranes, rings and cymbals, in all of which the normal nodal system consists of combinations of circles and diameters.

§ 1. INTRODUCTION

ONE of the earliest nodal designs produced by means of solid carbon dioxide was that shown in figure 21 of the present paper. It was noticed that whereas 12 nodal lines can be counted at the centre, there are 20 round the circumference. The figure appears to be a variant of either a 0/10 (no circles, ten diameters) figure or of a 1/6 (one circle, six diameters) figure, or really a combination of these two simple figures. This conclusion, arrived at visually, was subsequently confirmed by aural means when it was found that the vibration frequencies of the two simple modes of the compounded mode were practically identical.

This early observation supplied the key to the explanation of all the other figures that have been produced. The grouping of these figures is shown in the two plates; it was not completed until the knowledge regarding the normal vibrating modes which has been described in part 1 was available.

The combination of two simple modes is made possible by a slight want of uniformity in the plate under observation. Thus in the present experiments the thickness of the 30.47-cm.-diameter plate was found to vary from 2.040 to 2.020 mm. and that of the 25.71-cm.-diameter plate from 2.017 to 2.030 mm. This departure from exact symmetry causes a divergence of free periods^(1a) and renders determinate the positions of the nodal diameters. The nodal figure will therefore vary according to the position of excitation, and it will be possible for two or more normal modes of

neighbouring periods to coexist in any proportions. This compounding of modes may be compared with that which is always possible in the case of square plates^(1b) where two fundamental modes, at least, have equal periods.

§ 2. TECHNIQUE

The plates were treated in the manner described in part 1, § 2. Both the bowing and the solid-carbon-dioxide methods of producing vibrations were used, the former for exciting at the edge, and the latter for exciting at other points on the surface of the plate. The figures shown at 1, 2, 4-6, 9, 17, 20, 23, 24, 27, 34-36, 48 and 55-58 in plates 1 and 2 were produced by bowing.

§ 3. COMPOUNDED NORMAL MODES

The groups of figures, arranged as far as possible in ascending order of tone, are shown in the two plates, and a summary of results is given in table 1.

Table 1. Compounded normal modes of vibration, figures 1 to 58

		Frequencies relative to o/2 tone = 1	R*
Plate 1:	Two modes		
Figures 1 to 3	o/4, 1/1	4·10, 3·99	3
4 to 6	o/5, 1/2	6·19, 6·79	3
7	o/8, 1/4	15·1, 13·8	4
8 to 14	o/9, 1/5	18·8, 18·1	4
15 to 28	o/10, 1/6	23·0, 23·1	4
29 to 31	o/11, 1/7	27·6, 28·6	4
32	o/12, 1/8	33·0, 34·7	4
33	o/13, 1/9	38·0, 40·0	4
—	o/17, 1/12	65·5, 63·0	5
Plate 2:			
Figures 34 to 36	o/7, 2/1	11·7, 11·74	3
37	o/8, 2/2	15·1, 16·1	3
38, 39	o/11, 2/4	27·6, 27·1	3·5
40, 41	o/12, 2/5	33·0, 33·4	3·5
—	o/16, 2/8	58·0, 56·0	4
42 to 47	o/14, 3/4	44·5, 43·0	3·3
48	o/13, 4/1	38·0, 37·0	3
49, 50	1/9, 2/6	40·8, 40·5	3
51, 52	1/10, 2/7	47·5, 47·7	3
	Three modes		
53, 54	o/12, 1/8, 2/5	33·0, 34·7, 33·4	4, 3
55, 56	o/17, 1/12, 2/9	65·5, 63·0, 65·0	5, 3
57	1/10, 2/7, 3/5	47·5, 47·7, 50·5	3, 2
58	1/10, 2/7, 5/0	47·5, 47·7, 47·0	3, 2·3

* Number of nodal diameters which raise the pitch by approximately the same amount as one nodal circle.

The o/10, 1/6 group (figures 15-28), of which figure 21 has already been mentioned, will first be considered in some detail.

It will be seen that the two simple modes, $0/10$ (obtained on Prof. Andrade's uniform plate mentioned in part 1) and $1/6$, are shown in figures 15 and 28 respectively. Between these figures there are two columns of compounded nodal figures in which it is interesting to compare the two different developments of design. The distorting effect of an additional clamp at the edge is shown in figure 27, which is only just recognizable as belonging to the group.

For the recognition of the basic normal modes of more complicated figures, it will be useful to record from observations made on this group that (1) A hoop at the circumference, figure 20, is an indication of 2 diameters in one of the constituent normal modes and of a circle in the other. (2) A loop from the centre, figure 25, indicates 2 diameters and 1 circle of one of the modes. (3) A bend in a nodal radius, figure 22, is evidence of the presence of a nodal circle in one of the modes.

Passing now to the other figures shown in plates 1 and 2, it may be remarked that the crown-like figure 3 ($0/4$, $1/1$) is frequently obtained when a small plate is held at a node between the thumb and first finger and the solid carbon dioxide is applied in the middle of one of the two vibrating central portions; the plate is not quite free, and both this figure and figure 2 may be compared to the inverted Chladni figure 101*b*, part 3. An eccentric circular clamp was used in the production of figure 1. Figures 4 to 6, in the $0/5$, $1/2$ group, are again typical of plates which are unsupported so as to allow of entirely free vibration. The first two, if inverted, may be compared with Chladni's figure 102*b*. The component modes of figures 8 to 14 (in the $0/9$, $1/5$ group) are easily recognized, but the flatness of the hoop in figure 13 should be noted as this makes it easy to recognize the $0/8$, $1/4$, figure 7, and the component parts of several other nodal patterns.

The varying designs in the $0/14$, $3/4$ group, figures 42 to 47, may be noted, and especially the meaning of such wavy lines as are found in the last two figures, some of which indicate 3 and some 4 diameters. It is then possible to recognize the component modes of figures 37 and 38 or 39. Figure 48 (characterized as $0/13$, $4/1$) is the most important nodal design in connexion with the study of Chladni's own drawings, part 3, and shows the *Biegungen* or bendings which are so characteristic of many of them. Comparison with figures 36, 45, 44, 43 and 42 shows that each bending from crest to crest indicates two radii of one of the combining modes. Figure 58 should also be studied in this connexion; the waviness of the lines is typical of bow-excitation, and from them traces of the $1/10$ and $2/7$ modes can be recognized superposed on the predominating $5/0$ mode. Three simple modes are combined in figure 54, of which $2/5$ can be recognized by looking at the central portion of the plate $0/12$ and by looking at the circumference, while the presence of $1/8$ is seen by omitting diameters (indicated by 4 hoops at the circumference) and adding a circle in their place. The plate was clamped as in figure 56 ($0/17$, $1/12$, $2/9$), and excited by bowing. The double bend of some of the radii in figure 57 ($1/10$, $2/7$, $3/5$), indicative of two circles, may be noted; it is also possible to see a trace of the $3/5$ mode in this nodal design.

The above conclusions regarding the combination of simple modes, which have been arrived at mainly by inspection of the nodal systems, are confirmed by finding

that the vibration frequencies of the designs belonging to any one group are intermediate between the two nearly equal frequencies of the parent modes. The summary of results which is given in table 1 includes also several later observations on higher compound nodal designs which were not photographed. The numbers in the last column give the number of nodal diameters which raise the frequency of vibration by as much as does one nodal circle, and are of importance in connexion with the argument set out in § 4 of part 1.

Superposed sand figures. The four figures, 59 to 62, shown at the bottom of the right-hand side of plate 2, differ in character from those already considered, and were obtained by chance when it happened that the plate was excited a second time by means of solid carbon dioxide in such a way as to produce a second sand pattern, which because of its geometrical similarity did not disturb much of the first pattern. Figure 59 appears to be a 0/6 nodal pattern superposed on a 1/1 pattern, and figure 60 a 1/9 pattern superposed on a 2/3 pattern. Figure 61 is 0/9 superposed on 2/4, assuming the amplitude of the second vibration to have been insufficient to disturb the sand of the inner circle. Figure 62 is possibly made up of 0/9 with a compound vibration 1/10, 3/4 superposed on it. The vibration frequencies (which are unequal) of the two patterns do not of course enter into the elucidation of such figures.

§ 4. FURTHER REMARKS

Comparison with nodal designs of damped and forced vibrations. It is interesting to compare the present results with a large number of drawings made by Elsas⁽²⁾ showing the nodal figures obtained on damped circular membranes, the vibrations of which were forced. In such a case, as was shown subsequently by Debye⁽³⁾, it is possible for two neighbouring natural modes to combine because of the flatness of resonance. In fact a simple mode is never produced singly. Franke⁽⁴⁾ has followed up this work with a study of the forced vibrations of clamped circular plates, and a paper by Shünemann⁽⁵⁾ may also be mentioned in this connexion. Though the figures are of course not the same as those given by free circular plates, yet since they are also those of a system of revolution they often bear a strong resemblance to some of them. There is, I think, evidence of forcing or at any rate external damping in many of the figures obtained by Colwell⁽⁶⁾ on free circular plates by means of a magnetostriction oscillator. The exciter has its own period, and a very nice adjustment of frequency is necessary in order to avoid an element of forcing. The method of support also affects the result. The somewhat square circle and the dumb-bell-shaped central nodal curve in some of Colwell's figures can be found also among the nodal figures yielded by Elsas's forced vibrations.

Vibrations of circular membranes. The principle of composition that has been developed in the present paper is evidently applicable to circular membranes, and assuming that the relative actual frequencies are the same as those given theoretically by a table of the roots of Bessel functions of the first kind, the following combinations among the lower partials appear probable: 0/2, 2/0; 0/5, 2/2; 3/2, 4/0. As in the case of plates it would seem that no two modes have exactly the same period,

but since the overtones are very numerous (as may be seen from table 2, where the number of overtones in given intervals of several different vibrating systems have been compared) and the vibrations are relatively damped, compounded modes should occur fairly frequently. Any inequality of tension over the surface of the membrane will cause distortion, and the recent figures due to Schiller⁽⁷⁾ have the irregular features of figure 27 of the present paper, which was distorted by means of a clamp. The following compound modes can however possibly be recognized in his figures 4*a*, 4*b* and 4*c* respectively: 0/4, 1/2; 0/5, 2/2; 0/6, 2/2; and 0/3, 1/0 in his figure 5.

Table 2. Number of overtones in given intervals

Octaves	1	2	3	4	5	6	7	Source of information
Strings	2	4	8	16	32	64	128	Present observations. Tables and Franke. From roots of Bessel Functions of first kind.
Free plates	1	4	8	14	27	51	84	
Clamped plates	1	4	7	18				
Membranes	2	10	44	c. 157				

Comparison with circular plates clamped round the edge. Similarly it is possible to surmise which vibrating modes should combine in plates which are clamped round the edge, as is done in table 3, in which a few suggested combinations are placed by the side of the actual combinations that have been obtained with free circular plates. It may be noted, for example, that the 0/5 figure which we have seen compounded with a 1/2 mode in figures 4 to 6 above should, in the case of the clamped plate, combine with a 2/0 mode.

Table 3. Compounded normal vibrating modes

Free circular plate, experimental	Clamped circular plate, suggested
0/4 (4.10), 1/1 (3.99)	
0/5 (6.19), 1/2 (6.79)	0/5 (8.88), 2/0 (8.72)
	0/6 (11.27), 2/1 (11.8)
0/7 (11.7), 2/1 (11.74)	0/7 (13.8), 1/4 (13.7)

The frequencies of the free plate are given relatively to that of its gravest 0/2 mode, taken as 1, and those of the clamped plate are given relatively to that of its gravest 0/0 mode, taken as 1. It has been calculated⁽⁸⁾ that the frequency of the 0/0 mode of the clamped plate is approximately 1.92 times the frequency of the 0/2 mode of the free plate.

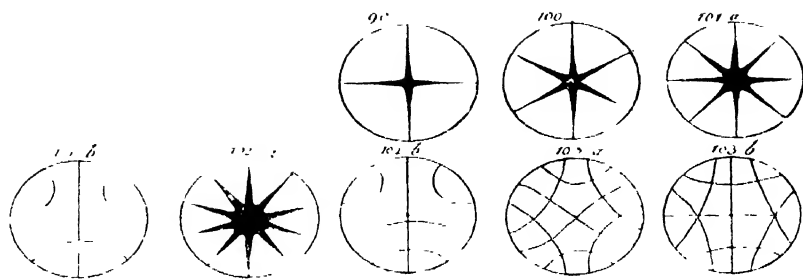
Cymbals. A few preliminary experiments with cymbals, kindly lent by Messrs Boosey and Hawkes, show that both the normal modes, in which the radii of the nodal circles and relative frequencies depend upon the type of cymbal, and also compounded modes can be produced. It will be interesting to continue these experiments, since the results could scarcely be obtained by analytical methods. The main difficulty is to obtain a powder which, though sufficiently mobile, will not slide off the plates.

§ 5. CONCLUSIONS

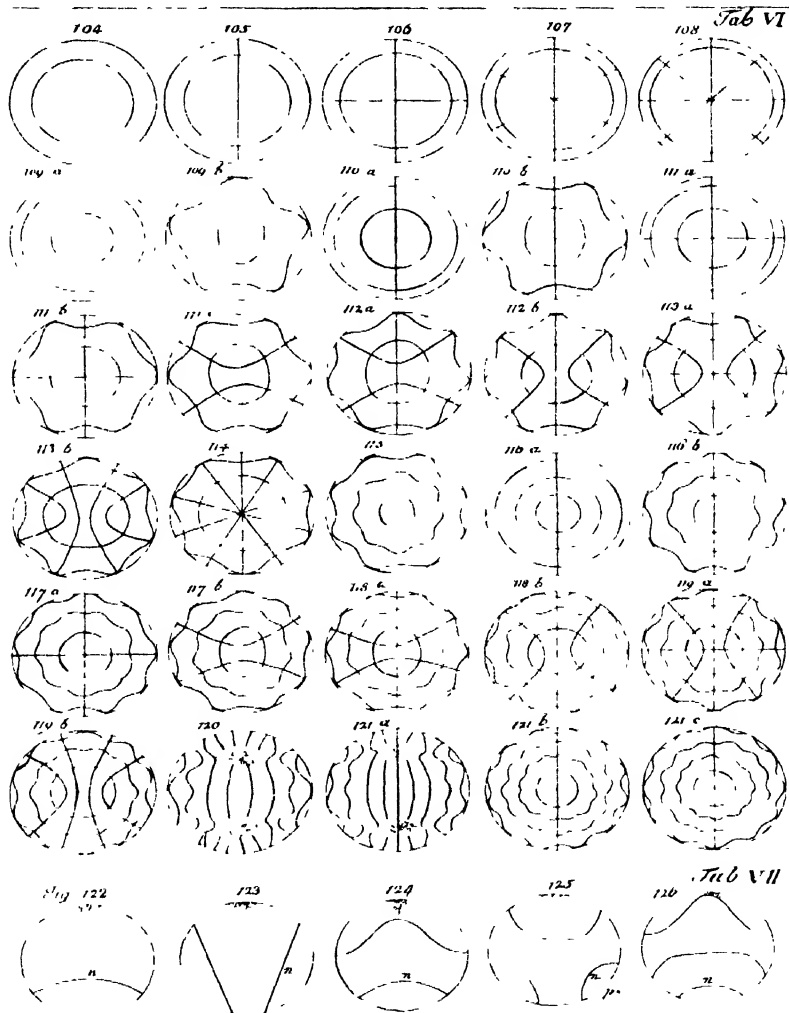
All nodal designs, other than those corresponding to the normal modes of vibration, which can be produced on free circular plates or on other systems of revolution result from the combination of two or more normal modes of nearly equal period. This compounding of modes is made possible by the want of uniformity which generally exists in actual plates, and it is also made easier by an increase in the damping of the vibrations. The most usual cause of want of uniformity is a small variation in thickness. Another possible cause is variation of elasticity of the material in plates which have been rolled in one direction.

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Chladni's Akustik



Figures 99-126 from Chladni, *Die Akustik*.

VIBRATIONS OF FREE CIRCULAR PLATES. PART 3: A STUDY OF CHLADNI'S ORIGINAL FIGURES

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ABSTRACT. The complete set of figures which Chladni produced on circular plates has been examined. It has been found that a second subsidiary normal vibrating mode, the nodal system of which consists of diameters, is in many of the figures compounded with a principal figure of nearly identical period. The manner of support and the manner of excitation make such combinations likely.

§ 1. CHLADNI'S ORIGINAL FIGURES ON CIRCULAR PLATES

THE *Entdeckungen über die Theorie des Klanges* which was published by Ernst Florens Friedrich Chladni in 1787 contains seventy-five copper-plate figures of his drawings of nodal lines produced on circular plates. Forty-three of these figures are reproduced in *Die Akustik* (1802, second edition 1830). They are shown in plates 1 and 2 of the present paper and were obtained at the Royal Institution through the kindness of Mr R. Cory the Librarian. The rest of the figures in the *Entdeckungen über die Theorie des Klanges* are, with but few exceptions to which reference will be made below, similar in character to those shown in plates 1 and 2. The study that has already been described in parts 1 and 2 of the present paper make it possible to see that most of the figures are a combination of two normal modes of vibration having nearly equal periods.

Of the single simple modes the highest number of diameters shown is five. Chladni, of course, produced a greater number of diameters than this, and his table of frequencies extends as far as eight diameters. He gives drawings for one and for two nodal circles; this is probably quite as much as could be managed by means of a bow applied at the edge of the plate. The highest single mode shown is that of figure 116*a*, which is of the 3/1 type. The relative frequency of this mode, according to table 1, of part 1, is 22.7.* There is considerable distortion in some of the earliest and latest figures, and this is no doubt due to a want of freedom in the manner in which the plate is supported.

The remaining figures all show a greater or smaller number of *Biegungen* or bendings in the nodal circles. Chladni paid special attention to these and gave a table⁽¹⁾ of the number generally associated with each figure, which number can also be counted directly on the figures reproduced in the present paper.

* It has been shown in part 1, § 4, that the relative frequencies are affected by the value of Poisson's ratio, so that the figures quoted here and below apply only approximately to glass plates.

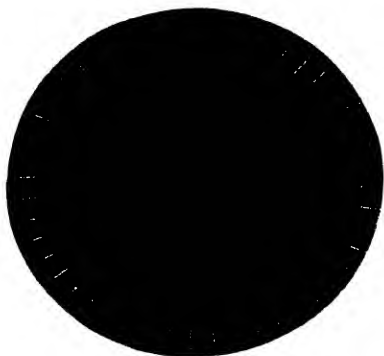
Figure 48 of part 2 of the present paper, which is a $0/13$, $4/1$ figure, was produced by bowing. It is of the same type as Chladni's, and each bend, or distance from crest to crest, in the wavy nodal circles evidently indicates the presence of two diameters of one of the combining modes, so that counting round the whole circle the number of bends in a figure such as 115 shows that an 8-diameter mode has combined with a 3-circle mode. In the case of figures which include obvious diameters, whether straight or curved, it has been found that the *Biegungen* diameters must be added to these in order to obtain the second vibrating mode.

Table 1 has been compiled according to this rule, the predominating mode being printed in black numerals while the frequency relative to that of the gravest mode, $0/2$ (obtained from table 1 of part 1), is given in brackets. References to figures given in part 2 are followed by the letter *W*.

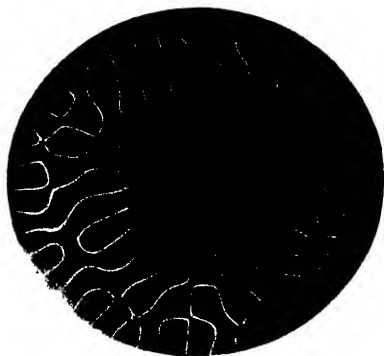
Table 1. Composition of Chladni's figures on circular plates

Figure	Modes and relative frequencies	Remarks
101 <i>b</i>	$0/4$ (4.1), $1/1$ (3.99)	Cf. figure 2, <i>W</i> , inverted, and also the less regular figures 125, 126 below
102 <i>b</i>	$0/5$ (6.19), $1/2$ (6.79)	Cf. figures 4-6, <i>W</i> , inverted
103 <i>a</i> , <i>b</i>	$0/8$ (15.1), $2/2$ (16.1)	Cf. 37, <i>W</i>
109 <i>b</i>	$2/0$ (7.50), $0/5$ (6.19)	Chladni states that this was the only case in which he noted that the pitch was lower than that of the corresponding regular figure, here 109 <i>a</i> . There are 6 instead of 5 <i>Biegungen</i> in the corresponding <i>Entdeckungen</i> figure, $2/0$ (7.50), $0/6$ (8.8)
110 <i>b</i>	$2/1$ (11.74), $0/6 + 1 = 0/7$ (11.7)	Cf. 36, <i>W</i>
111 <i>b</i> , <i>c</i>	$2/2$ (16.1), $0/8$ (15.1)	Cf. 103 <i>a</i> , <i>b</i> and 37, <i>W</i>
112 <i>a</i> , <i>b</i>	$2/3$ (21.2), $0/7 + 3 = 0/10$ (23)	
113 <i>a</i> , <i>b</i>	$2/4$ (27.1), $0/7 + 4 = 0/11$ (27.6)	Cf. 38, 39, <i>W</i>
114	$2/5$ (33.4), $0/7 + 5 = 0/12$ (33)	Cf. 40, 41, <i>W</i>
115	$3/0$ (16.4), $0/8$ (15.1)	
116 <i>b</i>	$3/1$ (22.7), $0/9 + 1 = 0/10$ (23)	
117 <i>a</i> , <i>b</i>	$3/2$ (29.4), $0/9 + 2 = 0/11$ (27.6)	
118 <i>a</i> , <i>b</i>	$3/3$ (36.3), $0/10 + 3 = 0/13$ (38)	
119 <i>a</i> , <i>b</i>	$3/4$ (43), $0/10 + 4 = 0/14$ (44.5)	Cf. 42-47, <i>W</i>
120	$4/0$ (29.1), $0/12$ (33)	In this and several neighbouring figures, and in those showing hyperbolic diameters, the imperfect freedom of the vibrations is specially manifest
121 <i>a</i> , <i>b</i> , <i>c</i>	$4/1$ (37), $0/13$ (38)	Cf. 48, <i>W</i>
122	Less free, distorted $0/2$	
123, 124	Distorted $0/3$ (2.29)	
125, 126	Distorted $0/4$ (4.10) and $1/1$ (3.99)	

Additional figures in the Entdeckungen über die Theorie des Klanges. There are several more variants of the $0/5$ (6.9), $1/2$ (6.79) nodal figure to be seen in Chladni's earlier publication. The remaining figures are similar to those already considered but are compounded of higher partials, the last of which is a $7/0$, $0/22$ (110) combination evidently made on a plate which was not quite free.

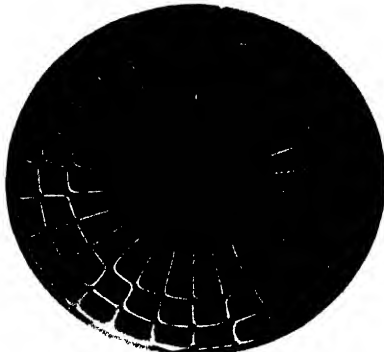


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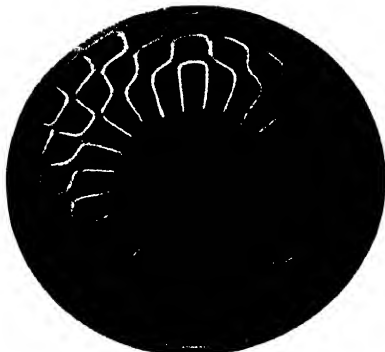


2

Figures 1, 2. Plate excited at the edge with a bow.



4



6

Figures 3 to 6. Plate excited between the centre and the edge with solid carbon dioxide; see table 2.

§ 2. NOTE ON METHODS OF PRODUCING VIBRATION IN PLATES

The six figures of plate 2 which were produced on a centrally supported plate of diameter 46.2 cm. and thickness 2 mm. illustrate the possibilities of producing higher partials by means of a bow or of solid carbon dioxide. The first two figures were made with a small violin bow plentifully supplied with powdered resin, and the last four with solid carbon dioxide which was applied between the centre and circumference of the plate. Data regarding these figures are given in table 2. The essential freedom of these two methods of excitation is shown by the single-mode nodal designs of figures 1, 3 and 4.

Table 2

Figure	Nodal design	Approximate frequency (c./sec.)	Approximate frequency relative to that of 0/2 mode
	Single mode		
1	0/24	4200	127
3	7/2	5300	160
4	3/13	5100	154
	Compounded modes		
2	0/23, 3/11	3900	118
5	5/2, 1/12, etc.	2080	65
6	3/12 (0/25)	4360	130

The difference in character between the decorative designs produced by excitation at the edge and near the centre respectively, is specially noticeable in figures 2 and 6. In figure 2 the 0/23 mode is combined with a 3/11 mode of smaller amplitude, while in figure 6 a 3/12 mode is combined with a 0/25 mode of very much smaller amplitude. There is a threefold motif in both figures which are very interesting to compare.

It is evident that by varying the point of application of the solid carbon dioxide, and by the appropriate use of a divider to introduce constraints and damping, it should be possible to obtain a large number of very beautiful designs.

The figures may be compared with one of Colwell's high-frequency figures^(a) produced with a magnetostriction oscillator, in which an 8/1 or 9/1 component is, I think, present. The frequency of this figure is stated to be some submultiple of 15,000 c./sec.; the size of the circular plate used is not specified.

An exhaustive reference to electrical methods of producing Chladni figures cannot be made here, but a brief mention of some purposes for which they have been employed when the two simpler methods could not be used may not be out of place. Thus Wood and Smith⁽³⁾ and Colwell and Hall⁽⁴⁾ have employed a magnetostriction oscillator to produce large numbers of nodal circles, the former for the purpose of determining the velocity of sound in non-metallic as well as in metallic circular sheets. Wood⁽⁵⁾ has also used the same method to excite small circular discs. Franke⁽⁶⁾ has produced forced oscillations in clamped circular plates. Andrade and Smith⁽⁷⁾

have used an electromagnet in order to control the amplitude of vibration of steel plates in their study of the manner of formation of sand figures. In this last connection it is interesting to compare such figures as 1 and 3 of plate 2, where in the first figure the amplitude of vibration is small except round the edge, while in figure 3, the plate is vibrating vigorously over its entire surface.

The main purpose of this concluding section, however, is to draw attention to the very simple and effective methods of excitation which continue to be available for most general purposes—the bowing method for producing diameter figures and decorative figures of a specified type, and the solid-carbon-dioxide method for producing not only these but also the circle and circle-diameter figures and the large variety of designs which can be obtained by altering the position of excitation over the surface of the plate.

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A NOTE ON THE OPTIMUM COUNTING-TIME FOR MEASURING THE INTENSITY OF A RADIOACTIVE SOURCE

By J. TANDBERG

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ABSTRACT. When the intensity of a radioactive source is measured by means of a Geiger-Müller counter, maximum accuracy is obtained by continuing the counting for a finite time which depends on the average life of the radioactive source and on the intensity of the background interference.

WHEN particles from a radioactive source are counted by means of a Geiger-Müller tube a certain background of adventitious impulses will always be present. If the period of the source is a short one it is of no use to extend the counting for a long time, since the natural fluctuations of the background will have a detrimental influence on the accuracy of the result. In figure 1 the straight line *A* represents the mean progression of the number of impulses counted, as a result of the background alone. Curve *B* may represent an actual count, involving the fluctuations of the background.

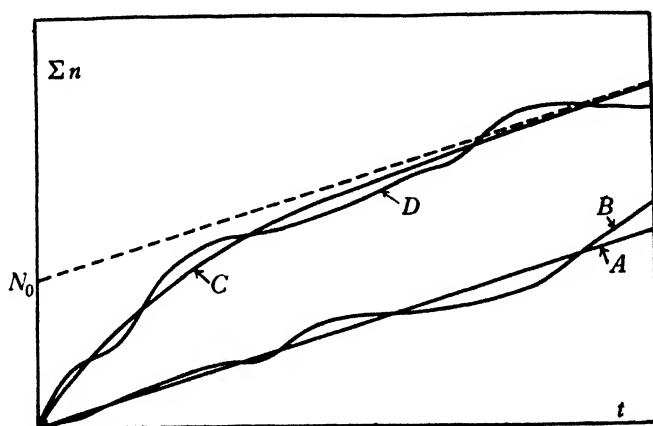


Figure 1.

The smooth line *C* represents the ideal counting of particles from a weak radioactive source, including the background, such as would occur if the fluctuations were negligible. The irregular curve *D* around *C* represents an actual counting series, inclusive of the fluctuations. It is obvious that if we wish to count the total quantity of particles emitted from the radioactive source during a very long time,

we shall not be helped by means of an extended counting series, because the fluctuations will soon cause the curves D and B to be confused. For a very short series, on the other hand, the fluctuations of the source itself may easily predominate and the result will accordingly be uncertain. An optimum counting-time is therefore to be expected.

Supposing we have an unknown number N_0 of impulses, latent at the beginning, the decay constant λ and the background of b impulses per minute being known,

20

$$\frac{N_0 \lambda}{b}$$

15- 4

10

Figure 2.

we shall get during t minutes $N_0(1 - e^{-\lambda t}) \pm \zeta$ impulses from the source and $bt \pm \sqrt{bt}$ impulses from the background. Here the mean number ζ of fluctuations is determined by the expression:

$$\zeta^2 = Z(1 - Z/N_0) = N_0(e^{-\lambda t} - e^{-2\lambda t}),$$

where Z stands for the first of the above expressions.

Thus we have during t minutes a total number of impulses:

$$\Sigma n = Z + bt \pm \sqrt{(\zeta^2 + bt)}.$$

In order to obtain the least erroneous value of N_0 we will set out to find the

time t^* for which the mean relative fluctuations $1/Z \sqrt{(\zeta^2 + bt)}$ shows a minimum. We proceed to investigate the square of the expression and thus obtain the function

$$f(t) = \frac{1}{Z^2} \left\{ Z \left(1 - \frac{Z}{N_0} \right) + bt \right\} = \frac{1}{N_0} \left\{ \frac{e^{-\lambda t}}{1 - e^{-\lambda t}} + \frac{bt}{N_0 (1 - e^{-\lambda t})^2} \right\}.$$

Making the first derivative $f'(t)$ equal to 0 and transforming the expression we get

$$\frac{N_0 \lambda}{b} = e^{\lambda t^*} - \frac{2\lambda t^*}{1 - e^{-\lambda t^*}}.$$

An investigation of the second derivative will confirm that t^* corresponds to a minimum of $f(t)$.

Denoting $\lambda t^* = \Theta$ we may regard Θ as the optimum time of counting, expressed in terms of the average life ($1/\lambda$) of the radioactive substance.

Now $N_0 \lambda$ represents the initial intensity of the source, corrected for the effect of the background. Thus the quotient $N_0 \lambda / b$ may be considered as the relative initial intensity of the radioactive source in terms of that of the background. The graph in figure 2 gives the relation between $N_0 \lambda / b$ and Θ for small values of Θ . If we consider a numerical example with radioactive indium, for which $\lambda = 0.01274 \text{ min}^{-1}$, having an initial activity equal to the background, it will be seen that it is of no use to continue the measurement longer than $\Theta = 1.6$ or about 2 hours. An extended counting of impulses would give results of decreasing accuracy.

THE RATIO OF THE MASSES OF THE FUNDAMENTAL PARTICLES

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ABSTRACT. A discussion of the nature of the equations of the quantum theory, based upon the theory of relativity, having indicated that difficulties of a fundamental character will arise when dimensions less than the electron-radius are concerned, it is pointed out that the idea that such dimensions are not observable must be included in a geometrical description in physics. The electron-radius is thus the minimum length we discover in our measurements relating to the interaction of particles. But the principle of minimum proper time applied to the track of a heavy particle M_0 shows that the particle is in effect a time scale whose finest division is h/M_0c^2 . In the theory of relativity the conception of a minimum length e^2/m_0c^2 becomes equivalent to the conception of a minimum interval of proper time e^2/m_0c^3 . The argument shows that these two intervals are of the same order of magnitude and leads to a simple relation between the mass ratio of the proton and electron and the fine-structure constant.

IN a communication published in these *Proceedings*⁽¹⁾ a short time ago, Dirac's quantum equation was developed from a new point of view. The details of the development are set forth in that communication, but the basis of the procedure may be briefly stated here. The underlying idea is that the quantum equation, written down for the case of a single charged particle in an electromagnetic field in the form required by the theory of relativity, is the representation of a law of natural gauging. The procedure is nothing more than an appeal to mathematical form based on Weyl's metrical theory and upon Eddington's generalization of it. From the physical point of view it is preferable to Weyl's system of gauging in that the idea of parallel displacement which has to be included in the geometrical and metrical description of the physical world can be correlated with actual displacements taking place in that world. The natural law of gauging deduced from the equation gives to the conception of parallel displacement the physical content lacking in the theory of Weyl.

The change of length which a vector undergoes in such a displacement was shown to be

$$\frac{\delta l}{l} = \frac{2\pi i}{h} \left(m_0 c^2 \delta \tau - \frac{e}{c} \phi_m \delta x^m \right) \quad \dots\dots(1).$$

We are here thinking of a track along which a charge e associated with a rest mass m_0 is travelling. A vector of length l with one end on the track is displaced

parallel to itself so that the co-ordinates of the end change by $(\delta x^1 \delta x^2 \delta x^3 \delta x^4)$. $\delta\tau$ is the element of proper time corresponding to the displacement. ϕ_m is a typical component of electromagnetic potential.

Some conclusions with regard to the limit of application of the theory were given at the end of the previous communication. The question has been further discussed⁽²⁾ and it has been shown that difficulties of a fundamental character are encountered when we attempt to solve any problem in which ultimate units e of electric charge lie closer together than a distance of the order e^2/m_0c^2 , m_0 denoting the rest mass of the electron. The discussion suggests that within a domain of such linear dimensions our customary conception of space and time breaks down, and that it would be surprising if, with this conception, smaller distances made their appearance in the physical world. Thus if we adopt a geometrical description of the physical world and if we take this point into consideration, the postulate must be included that points within such small domains are indistinguishable from one another. There appears in this way a smallest dimension l_0 which we describe as e^2/m_0c^2 , where m_0 is a constant having the dimensions of mass. Introduced in this way m_0 is no longer subject to the limitations which characterize it when we recognize it as the mass of a particle to which we give a definite structure. But if we can imagine ourselves starting out with a constant having the dimensions of mass and introduced in this way, its appearance in any equation would naturally suggest to the mind of a physicist trained in the laws of mechanics the existence of a particle of mass m_0 . If the length, l_0 , has the fundamental significance which we now suggest, it will be certain to be discovered in our investigations in physics and it may appear in a connexion not necessarily associated with the electron. Prof. A. March⁽³⁾, quite independently of these discussions, has made the assumption that in a four-dimensional world there is no means of distinguishing between points separated in space-time by a distance less than e^2/m_0c^2 . This view he developed in two papers on "The geometry of smallest spaces", but later he modified his views somewhat in the foundation of a statistical metric in which the idea that an electron is not to be defined within a sphere of the above radius l_0 is an essential feature. He shows that the difficulties associated with the self-energy of the electron can in this way be avoided, and in a paper on the gravitational energy of the photon⁽⁴⁾ he points out the occurrence of the length l_0 in a phenomenon which has nothing to do with the electron.

In the author's earlier communication already referred to⁽¹⁾ the principle of minimum proper time was deduced from equation (1). This principle, originally developed from the old quantum conditions relating to action and momentum⁽⁵⁾, has been established in a variety of ways⁽⁶⁾. It states that when a neutral particle of rest mass M_0 is considered, it is impossible to associate with its motion any interval of proper time less than h/M_0c^2 ; and the same is true of a charged particle in a weak field. Both this principle and the idea that l_0 is the smallest length occurring in the physical world are contained in the gauging law (1), for as we have shown before^(1,2) the quantum conditions are replaced by the rule that in any parallel displacement which has a physical counterpart the change δl is always zero; or in

other words, the quantity in the brackets on the right-hand side of (1) is always an integral multiple of h .

We thus include in one quantum law two fundamental lengths h/m_0c and e^2/m_0c^2 .

This view of the nature of the length which we usually describe as the radius of the electron gives a new approach to problems which have been explained by assuming the existence of an elementary particle carrying a charge e , possessing mass m_0 , and of the form of a sphere of radius $k(e^2/m_0c^2)$, where k is of the order unity.

The alternative to the introduction of the electron as a particle is the idea that the smallest interval of proper time observable in the physical world is of the order e^2/m_0c^3 , where m_0 simply occurs as a constant of the dimensions of mass.

This particular magnitude arises, according to the usual conception, in a consideration of the interaction of fundamental particles with one another. To these fundamental particles we assign masses M_0 and m_0 , described as the masses of a proton or neutron and of an electron. For the present purpose it is not necessary to distinguish between the masses of the two heavy particles.

The principle of minimum proper time allows us to regard the particle of mass M_0 as a scale of time of which the smallest division is h/M_0c^2 .

This scale of time is sufficiently finely divided to enable us to measure h_0/c , so that the two intervals are of the same order of magnitude. This view may be expressed as an equation thus

$$\frac{h}{M_0c^2} = k \frac{e^2}{m_0c^3} \quad \dots\dots(2),$$

where k is of the order unity.

Thus in our calculations we shall be concerned with the mass ratio M_0/m_0 , where

$$\frac{M_0}{m_0} = \frac{2\pi}{k} \left(\frac{hc}{2\pi e^2} \right) \quad \dots\dots(3).$$

Experiments which measure M_0/m_0 , e , c and h , or the fine-structure constant $2\pi e^2/hc$ directly, will give the value of k .

If we use a particle description of the phenomena instead of the geometrical one, we shall describe the ratio as the ratio of their masses.

The relation (3) is satisfactory from the point of view of order of magnitude, if M_0/m_0 is the ratio of the mass of the proton to that of the electron.

One hesitates to go farther with this equation in order to deduce from it more than an equality of magnitudes, especially as the determination of k is not altogether satisfactory. But it is interesting to examine the agreement afforded by making use of a value of k which has been suggested by the view that we are dealing with an electron with a definite structure and satisfying certain energy relations. Values of k suggested by the classical theory are $\frac{3}{2}$ and $\frac{4}{3}$, according to the nature of the distribution of the charge. Fürth has attempted a calculation⁽⁷⁾ more in accordance with new quantum considerations. He has pointed out that it becomes difficult to consider an electron as a sharply defined structure and considers a length which he describes as an equivalent radius, the value of k according to him being $\frac{1}{2}\frac{5}{2}$.

We shall take this value since Fürth's calculation rests upon modern ideas, though according to our view the constant k must be independent of any theory about the structure of a particle.

With this value we obtain the agreement described below. But from a study of the literature on the values of the mass ratio and of the fine-structure constant it would appear that the last word has not been said upon this subject.

On one hand we have Eddington's suggestion that $hc/2\pi e^2$ is integral and equal to 137, and on the other the value 137.2 was suggested a few years ago. Recent contributions to the discussion suggest a value closer to 137, but in the opinion of some spectroscopists it is not yet possible to be certain of this value within a margin equal to 0.1.

A similar difficulty occurs with regard to the mass ratio. Recent contributions to the discussion appear to point to a value close to 1839, although there is one suggestion that the value is 1837.

These numbers serve to illustrate the agreement of the formula when Fürth's value is taken for k . For the lower number 137 the ratio is 1836.4 and for the higher value 137.2 the ratio is 1839.0.

Our object here is not to lay stress on the actual values obtained but to point out the simple relation between the mass ratio and the fine-structure constant, and the new character which the ratio acquires from the assumption of the existence of an indivisible scale of time.

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DISCUSSION

Mr J. GUILD. When surprisingly accurate numerical agreements, such as that given in the present paper, drop out of theoretical equations, it is wise nowadays to look carefully for the possibility of circular reasoning before accepting them as confirmation of the theory. The danger of this is now very great, owing to the impossibility of anyone carrying in mind more than a fragmentary précis of the large volume of literature that has been written round the few constants h , c , e , M_0 and m_0 . I think we can find an example of this danger in the present case. Flint's value of M_0/m_0 depends on Fürth's value of k . There are numerous assumptions in Fürth's paper which one might question if that paper were the subject of discussion, but as it is not we may take it at its face value in considering its bearing on the result of the present paper. On Fürth's theory, the quantity k must obey

the relation

$$M_0/m_0 + m_0/M_0 + 2 = hc/ke^2 \quad \dots\dots(A),$$

which is Fürth's equation (18) translated into the symbols of the present paper. All the quantities except k are known, so k can be obtained directly from this relation.

Fürth, it is true, then proposes a charge-distribution for the electron, and a definition of the electron radius, which gives the correct value of k very closely. This must not, however, be regarded as an independent estimate of k confirming the relation (A). This relation requires no confirmation on Fürth's theory. It is necessarily true in virtue of his previous treatment, whatever the structure of the electron may be. Had his proposed theory of electron structure not led to this value, that theory would have been at fault, and not relation (A), which is an integral part of his main theory and in fact implies the definition of the constant k as used by him.

As M_0/m_0 is nearly 2000, relation (A) implies that to within about 1 part in 1000

$$M_0/m_0 = hc/ke^2, \quad \text{or} \quad k = \frac{m_0}{M_0} \frac{hc}{e^2}.$$

If we insert this value of k in Flint's equation (2) we find that it reduces to an identity and will necessarily give back the same value of the proton-electron mass ratio that was put into it via Fürth's k .

Even were this not so, no value given by Fürth's theory can legitimately be quoted as confirming the hypothesis of the present paper, which is that distances less than e^2/m_0c^2 —about the diameter of the electron—are without physical significance. Fürth's structure of the electron, necessary to give a value of k consistent with relation (A), supposes a spacial distribution of charge both inside and outside the radial distance, and implies the applicability of ordinary integration with respect to distance right into the centre. Further, Fürth's theory, in common with many others, leads to a value of the radius of the proton which is to that of the electron in the inverse ratio of the masses; see his equations (4), (13) and (17), and his final numerical values. On the author's theory the world cannot accommodate anything smaller than an electron, certainly not an object only about a two-thousandth of its size, nor can distance possess integrability within the electron radius. He must reject these corner stones of Fürth's investigation, and with them of course Fürth's value of k , as incompatible with the theory he is seeking to establish.

The view that space and time lose their significance below certain limiting values is a purely metaphysical escape from the difficulties which confront mathematical analyses, of the types so far developed, when carried beyond these limits. Unless there is some conceivable experiment which would distinguish discontinuities in space or time, such discontinuities cannot exist even as a pragmatic hypothesis. No such experiment can be formulated. A conceivable experimental significance is the scientific criterion of actual or possible existence, and this really provides the answer to those who claim that the contemplation of mathematical form is a substitute for the contemptuously dismissed model. We cannot, even in imagination, construct an experiment from symbols. We have to conceive any experiment in terms of bits of reality, actual or hypothetical; not symbols but the

things to which the symbols refer; in other words, the constituents of a model. Any attempt to do this in the present case leads at once to logical contradictions. The author relates his minimum length and time by the relativistic formula in which space and time intervals are related by the boundary velocity c . What is the significance of velocity in a region of non-existent space and time? Further, how can we assess magnitudes in the ordinary space and time measures to such regions? The quantity l_0 is a length and yet is supposed to give a measure of the extent of some kind of region in which length is physically meaningless—some kind of gap in the structure of length. Similarly, we are given a time measure of the *duration* of gaps in the structure of time. Obviously if it were possible to conceive of discontinuities in space and time their extent would have to be measured in some other kind of dimensions altogether. We should have to conceive of space and time as having phenomenal existence *in* a continuum of some other kind. Discontinuity of space or time would then be conceivable and describable in terms of a metric appropriate to this non-temporal, non-spatial continuum. But the introduction of ideas of this kind with no empirical basis whatever has no justification. Space and time form the ultimate background of phenomena in all the equations of physics, which, therefore, cannot logically lead to the conception of discontinuity in that ultimate background itself.

We must avoid the tendency, when confronted with analytical difficulties, to invest nature with properties whose only function is to conceal our troubles. Eddington has warned us, in connexion with cosmic problems, of the danger of constructing a wall at the edge of the universe over which we can throw our unsolved problems. The quantum physicist does not carry his difficulties to the edge of the universe to dump them over the wall, but wants apparently to stuff them into holes in time and space. It is better to leave them lying about as a reminder that there is still work to be done in tidying up the unsolved problems of analysis.

AUTHOR'S reply. Mr Guild's criticism falls into two distinct parts, the first of which is concerned with arithmetical agreement and the second with considerations of a general character. I am not altogether out of sympathy with the opinions he expresses in the latter part, but he makes no statement which invalidates the basis on which the communication rests. This is that the description in terms of space and time is subject to conditions laid down by the quantum theory.

The first part of his criticism is more specific but the communication is concerned only with the equality of the orders of two magnitudes, not with arithmetical agreement. The value of k to which he refers is introduced merely to illustrate the agreement obtained, and it is expressly stated to be no part of the theory under discussion, which has so far not succeeded in deducing its value.

Mr Guild's remarks upon Fürth's paper, and in particular his reference to equation (A), show that he has misinterpreted its object. The constant k is calculated by Fürth independently of the ratio M_0/m_0 , just as it was calculated long ago in the classical theory without any reference to this ratio. Fürth's remark on equation (A) makes the point clear. "In order to obtain M_0/m_0 we need the value of k ."

ATOMIC SCATTERING FACTORS OF ALUMINIUM, POTASSIUM CHLORIDE AND COPPER FOR X RAYS

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ABSTRACT. The intensities of X-ray reflections from powders are placed on an absolute scale by comparison with reflections either from potassium chloride or from aluminium, the absolute values obtained by James and Brindley for these substances being taken as standard values. It is pointed out that the results obtained by standardizing with respect to aluminium are consistently about 10 per cent higher than those obtained when potassium chloride is used as the standard. New determinations of the scattering factors of potassium chloride and aluminium are made by the powder method, and it is shown that whereas the aluminium values agree well with the previous measurements made by James and Brindley, the new values for potassium chloride differ by an amount which explains the discrepancy mentioned above. The theoretical scattering factors of K^+ and Cl^- are recalculated on the basis of Hartree's latest wave functions, in which allowance for electron-exchange is made. Good agreement is found between the present measurements for potassium chloride and the theoretical results. The scattering factor of Cu^+ also is calculated with and without allowance for electron-exchange, and the results are compared with experimental data for metallic copper.

§ 1. INTRODUCTION

IN connexion with the absolute measurement of the intensities of X-ray reflections from powders by the methods described in the preceding paper, it was found necessary to re-examine the intensities reflected by potassium chloride and aluminium powders, since it is by comparison with reflections from these substances that reflected intensities from powders are placed on an absolute scale. For this purpose it is usual to take as standard values the absolute measurements of James and Brindley⁽¹³⁾ for potassium chloride and of James, Brindley and Wood⁽¹⁴⁾ for aluminium; these were obtained by the ionization method with large single crystals. Reflections from sodium chloride also are used as standards by some workers, and the measurements of James and Firth⁽¹²⁾ are then used. It has been found⁽¹⁾, however, that the results obtained by standardizing with respect to aluminium are consistently higher than those obtained when potassium chloride is used as the standard, the difference amounting to about 10 per cent in measurements of atomic scattering factors. These results suggested that incorrect values were being assumed for either the potassium chloride or the aluminium reflections, or both, and it was

considered essential, therefore, to discover the source of these discrepancies before either substance could be regarded as a satisfactory standard.

In the present paper, experimental values, obtained by the powder method, are given for the scattering factors of potassium chloride and aluminium for copper K_α radiation. The relative values for aluminium are shown to be in close agreement with the measurements made by James, Brindley and Wood for single crystals of aluminium and also with theoretical values based on the wave functions calculated by Hartree's method⁽⁴⁾. The absolute scattering factor of potassium chloride is then obtained from a comparison of the reflections from powdered potassium chloride with suitable reflections from powdered aluminium. The theoretical scattering factors of K^+ and Cl^- have been recalculated on the basis of the recent results of D. R. and W. Hartree⁽⁹⁾ for the electron-distributions of these ions, in which allowance for electron-exchange is made. The change in the scattering factors due to allowance for electron exchange is shown to be small but in such a direction as to increase the discrepancy with the previous measurements of James and Brindley. The new experimental values for potassium chloride, however, are in good agreement with the theoretical values.

The origin of the previous discrepancy is difficult to trace. It was clearly not due to anything of a fundamental nature, and the only explanation appears to be that it arose from some peculiarity or characteristic of the large crystals which were used in the experiments. This is also the opinion of Prof. James, who discusses the matter briefly in a note accompanying this paper.

Results are also given for the scattering factor of Cu^+ calculated with and without allowance for electron-exchange, and a brief comparison is made with experimental results for metallic copper.

§ 2. EXPERIMENTAL

The experiments were carried out with the X-ray camera and by the methods described in the preceding paper. The intensities were measured with a microphotometer by a null method of measurement. The films were developed and fixed under standard conditions, and the exposure times were so chosen that the maximum blackness of the lines came well within the range for which photographic blackness and X-ray intensity are proportional. Copper K_α radiation was used throughout the investigation. The relative intensity of reflection, I_r , is given by the relation

$$I_r/A \propto pF^2\phi(\theta) \quad \dots\dots(1),$$

where

$$\phi(\theta) = (1 + \cos^2 2\theta)/\sin \theta \sin 2\theta$$

and

$$A = \sin(2\theta - \alpha)/[\sin(2\theta - \alpha) + \sin \alpha].$$

Also p is the multiplicity factor for the reflection, F is the reflected amplitude per unit cell, θ is the Bragg angle of reflection and α the angle between the incident beam and the powder plate. For potassium chloride, $F = 4[f_T(K^+) + f_T(Cl^-)]$, where f_T denotes the effective atomic scattering factor at temperature T ; for aluminium, $F = 4f_T(Al)$. From relative measurements of I_r/A we obtain by means of relation (1) relative values of $f_T(K^+ + Cl^-)$, or $f_T(Al)$.

§ 3. RESULTS FOR ALUMINIUM

Since aluminium cannot be produced in a finely divided state by chemical means, a fine powder was prepared by filing and the finest particles were separated by means of a sieve having 350 meshes to the inch. The clear resolution of the $K\alpha_1\alpha_2$ doublet for high-order reflections indicates that there is little or no distortion in the filed powder. Any small distortion could be removed by suitable annealing, but this would be of doubtful value in the present investigation since removal of strain by annealing would probably be accompanied by crystal-growth and even if this is only small it may produce appreciable extinction effects. We have therefore preferred to use the powder in the unannealed condition; the results obtained suggest that any distortion produced by the filing has a negligible effect on the X-ray intensities.

Table 1. A comparison of the scattering factors of aluminium obtained from powder measurements, single-crystal measurements, and theoretical calculations

1	2	3	4	5	6	7	8	9	10
Spectra	Powder measurements			Single-crystal measurements (J., B. and W.)					Theoretical values of f_T for copper K_α radiation
	Copper K_α radiation			Molybdenum K_α radiation			Dis- pers- ion correc- tion	Copper K_α radiation f_T	
	I_r/A relative	f_T relative	f_T absolute	f_T ob- served	Extinct. correc- tion	f_T cor- rected			
	111	362.0	2.40	8.62	7.08	1.38	8.46	0.11	
200	166.0	2.22	7.98	6.63	1.33	7.96	0.11	8.07	8.13
220	100.0	1.86	6.68	—	—	6.58*	0.10	6.68	6.74
311	107.4	1.63	5.85	—	—	5.75*	0.10	5.85	5.91
222	31.2	1.58	5.67	5.25	0.27	5.52	0.10	5.62	5.69
400	—	—	—	4.46	0.19	4.65	0.09	4.74	4.80
331	48.4	1.16	4.16	—	—	4.06*	0.09	4.15	4.20
420	47.8	1.12	4.02	—	—	3.90*	0.09	3.99	4.04
422	53.7	0.95	3.41	—	—	3.32*	0.09	3.41	3.46
333	—	—	—	2.96	0.03	2.99	0.08	3.07	—
600	—	—	—	2.24	0.00	2.24	—	—	—
444	Unobtainable			1.57	0.00	1.57	—	—	—
800				1.08	0.00	1.08	—	—	—
555				0.87	0.00	0.87	—	—	—

* Values obtained by graphical interpolation.

The results are set out in table 1 and are compared with the absolute measurements made by James, Brindley and Wood for single crystals of aluminium, and also with the theoretical values calculated by the Hartree method. Column 1 gives the indices of the reflections, column 2 the observed values of I_r/A obtained from the powder photographs for copper K_α radiation relative to 100.0 for the 220 reflection, and column 3 the relative f_T values calculated by means of relation (1). The single-crystal measurements of James, Brindley and Wood are summarized in columns 5, 6 and 7; column 5 gives the observed f_T values, column 6 an extinction correction, and column 7 the f_T values corrected for extinction. The

extinction correction was obtained by assuming the theoretical f values derived by Hartree's method for the 111 and 200 reflections and was then calculated for the higher-order reflections by means of a formula due to Darwin. The f_T values for the 111 and 200 reflections are therefore the theoretical values modified by the appropriate temperature factor calculated from the experimental results given in the paper. The extinction correction falls off rapidly with increasing order of the reflections, and the higher-order f_T values are practically independent of the precise values assumed for the 111 and 200 reflections. In these experiments molybdenum K_α radiation was used and reflections were measured of higher order than can be obtained with copper K_α radiation. Before the powder measurements can be compared with the single-crystal measurements a small dispersion correction is necessary, and this has been calculated from the data given by Hönl⁽¹¹⁾. If $f_{\lambda \rightarrow 0}$, f_{Mo} and f_{Cu} are the scattering factors respectively for short waves, molybdenum K_α and copper K_α radiations, then in the usual notation,

$$f_{Cu} = f_{\lambda \rightarrow 0} - \Delta f_{Cu}$$

and

$$f_{Mo} = f_{\lambda \rightarrow 0} - \Delta f_{Mo},$$

so that

$$f_{Cu} = f_{Mo} - \Delta f_{Cu} + \Delta f_{Mo}.$$

For atoms vibrating at temperature T , we have

$$f_{T, Cu} = f_{T, Mo} + (\Delta f_{Mo} - \Delta f_{Cu}) e^{-M},$$

where $M = 0.01182 (h^2 + k^2 + l^2)$ according to the measurements made by James, Brindley and Wood. From Hönl's data, we have $\Delta f_{Cu} = -0.181$ and $\Delta f_{Mo} = -0.065$. The dispersion correction $(\Delta f_{Mo} - \Delta f_{Cu}) e^{-M}$, is tabulated in column 8 and the resulting f_T values for copper K_α radiation in column 9.

The relative f_T values from the powder measurements have been placed on an absolute scale by assuming f_T for the 220 reflection to be 6.68 as given by the single-crystal measurements; the results are given in column 4. The powder values in column 4 can now be compared with the single-crystal values in column 9; the agreement between the two sets of values is everywhere within the limits of experimental error and appears to justify the use of powdered aluminium as a satisfactory substance for standardizing the intensities of X-ray reflections from powders.

In column 10 are given the theoretical f_T values calculated by the Hartree method with the appropriate corrections for temperature and dispersion for copper K_α radiation. These values are based on the wave functions calculated by the self-consistent-field method, but without allowance for the effects of electron-exchange. In the case of K^+ , Cl^- and Cu^+ , allowance for electron-exchange has the effect of raising the scattering factors by a small amount, and presumably the effect will be in the same direction for aluminium. It is not possible to make any reliable estimate of the magnitude of the effect from the results for the other ions, but it will probably be small and will not affect very largely the good agreement between the calculated scattering factor and the observed values.

§ 4. RESULTS FOR POTASSIUM CHLORIDE

Finely divided potassium chloride powder was produced by dissolving metallic potassium in alcohol and passing hydrochloric acid gas or chlorine through the solution. Relative values of I_r/A were obtained in the manner already described and hence the relative values of f_T ($K^+ + Cl^-$); these are given in columns 3 and 4 of table 2. The absolute values of f_T were obtained by comparing the 420 and 422 reflections of potassium chloride with the 220 and 311 reflections of aluminium by the method of substituted powder layers described in the preceding paper; the results of the comparison are set out in the lower part of the table. The linear absorption coefficients of potassium chloride and aluminium for copper K_α radiation were taken as 243.5 and 131.8 respectively; the uncertainty in these values is probably less than 1 per cent, so that if both errors act in the same direction the final error in f_T for potassium chloride will not be greater than 1 per cent, since f_T depends on $\sqrt{\mu}$.

The scattering factor f for the atoms at rest, calculated by means of the usual equation

$$f_T = f e^{-M},$$

is tabulated in column 7. The temperature factor e^M in column 6 of the table is calculated from the expression

$$M = 1.689 (\sin^2 \theta) / \lambda^2,$$

where λ is in angstrom units. This expression is obtained from equation (10) of the paper by James, Brindley and Wood⁽¹⁴⁾ and is derived from experimental data.

To facilitate comparison with the theoretical scattering factors which are valid for sufficiently small waves such that $\lambda \ll \lambda_K$, the wave-length of the K absorption edge, it is necessary to correct the observed scattering factors for the effect of dispersion. According to Hönl's data, the dispersion correction has the value -0.66 ; in other words, to obtain f for short waves from the experimental values for copper K_α radiation, 0.66 must be subtracted. The resultant values are given in column 8 of table 2.

§ 5. THEORETICAL SCATTERING FACTORS OF K^+ AND Cl^-

For spherically symmetrical atoms, f is related to the radial charge-distribution $U(r)$ by the equation,

$$f = \int_0^\infty U(r) \phi^{-1} \sin \phi \, dr,$$

where $\phi = 4\pi r (\sin \theta) / \lambda$. The charge distributions of Cl^- and K^+ were calculated by Hartree's method of self-consistent fields by Hartree⁽⁴⁾ and by James and Brindley⁽¹³⁾ respectively. These calculations have been subsequently repeated by Hartree^(5,6) with considerably greater accuracy. In these calculations the effects of electron-exchange were neglected. Numerical calculations of atomic wave functions with allowance for electron-exchange were first made by Fock and

Petrashen⁽³⁾ for sodium, and by D. R. and W. Hartree^(7,8) for the normal and excited states of beryllium. They have since extended the work to Cl^- ⁽⁹⁾, Cu^+ ⁽¹⁰⁾ and K^+ . The results for K^+ have not yet been published and the writers are indebted to Prof. Hartree for permission to use them prior to their publication. In calculating

Table 2. Experimental results for potassium chloride

1	2	3	4	5	6	7	8
Spectra	$\sin \theta/\lambda$	I_r/A by experiment	f_T relative	f_T absolute copper K_α	e^M	f copper K_α	f $\lambda \rightarrow 0$
200	0.159	746.0	9.05	26.8	1.044	28.0	27.3 ₅
220	0.225	469.0	7.47	22.1	1.089	24.1	23.4 ₅
222	0.276	149.8	6.59	19.5	1.137	22.2	21.5 ₅
400	0.319	66.6	6.05	17.9	1.187	21.2 ₅	20.6
420	0.356	149.5	5.20	15.4	1.239	19.1	18.4 ₅
422	0.390	100.0	4.72	14.0	1.293	18.1	17.4 ₅
440	0.451	27.8	4.01	11.9	1.409	16.7 ₅	16.1
600, 442	0.478	56.1	3.69	10.9	1.471	16.0 ₅	15.4
620	0.504	39.4	3.46	10.2 ₅	1.535	15.7 ₅	15.1
622	0.528	35.5	3.18	9.4	1.602	15.0 ₅	14.4
640	0.574	33.8	2.80	8.3	1.746	14.5	13.8 ₅
642	0.596	71.1	2.60	7.7	1.822	14.0	13.3 ₅

Standardization data:

	f_T absolute	f_T re- lative	f_T absolute f_T relative
Potassium chloride 420 compared with aluminium 220 gives 15.49	15.44	5.20	2.97
Potassium chloride 420 „ aluminium 311 „ 15.39			
Potassium chloride 422 „ aluminium 220 „ 14.01	13.96	4.72	2.95
Potassium chloride 422 „ aluminium 311 „ 13.91			

Mean value of f_T absolute/ f_T relative, 2.96.

the difference between the scattering factors corresponding to charge-distributions obtained with and without allowance for electron-exchange, it is more convenient and accurate to use the difference equation,

$$f(\text{with exchange}) - f(\text{without exchange}) = \delta f$$

$$= \int_0^\infty \delta U(r) \phi^{-1} \sin \phi \cdot dr.$$

The numerical results for f , with and without allowance for electron exchange, and δf for K^+ , Cl^- and $(\text{K}^+ + \text{Cl}^-)$ are given in table 3. In the first column of the table, $(\sin \theta)/\lambda$ is expressed in terms of a_H , the radius of the one quantum orbit of hydrogen, and in the second column in angstroms, a_H being taken as 0.528 Å. The results are shown graphically in figure 1, where f is plotted against $(\sin \theta)/\lambda$; the ordinates for δf are on a scale ten times larger than the ordinates of f .

Table 3. Theoretical scattering factors of K^+ and Cl^-

$(\sin \theta)/\lambda$		f_b , without electron-exchange			f_a , with electron-exchange			$\delta f = f_a - f_b$		
Atomic units	A. ¹	K^+	Cl^-	$K^+ + Cl^-$	K^+	Cl^-	$K^+ + Cl^-$	K^+	Cl^-	$K^+ + Cl^-$
0.0	0.000	18.00	18.00	36.00	18.00	18.00	36.00	0.000	0.000	0.000
0.05	0.095	16.61	15.43	32.04	16.77	15.85	32.62	0.160	0.420	0.580
0.10	0.189	13.70	11.84	25.54	14.03	12.30	26.33	0.333	0.455	0.788
0.15	0.284	10.97	9.57	20.54	11.31	9.79	21.10	0.341	0.219	0.560
0.20	0.379	9.15	8.27	17.42	9.35	8.35	17.70	0.200	0.081	0.281
0.25	0.474	8.03	7.49	15.52	8.11	7.53	15.64	0.084	0.044	0.128
0.30	0.568	7.30	6.74	14.04	7.34	6.79	14.13	0.044	0.054	0.098
0.35	0.663	6.70	6.09	12.79	6.73	6.16	12.89	0.031	0.071	0.102
0.40	0.758	6.14	5.44	11.58	6.18	5.53	11.71	0.039	0.086	0.125
0.50	0.947	5.08	4.21	9.29	5.15	4.32	9.47	0.075	0.108	0.183

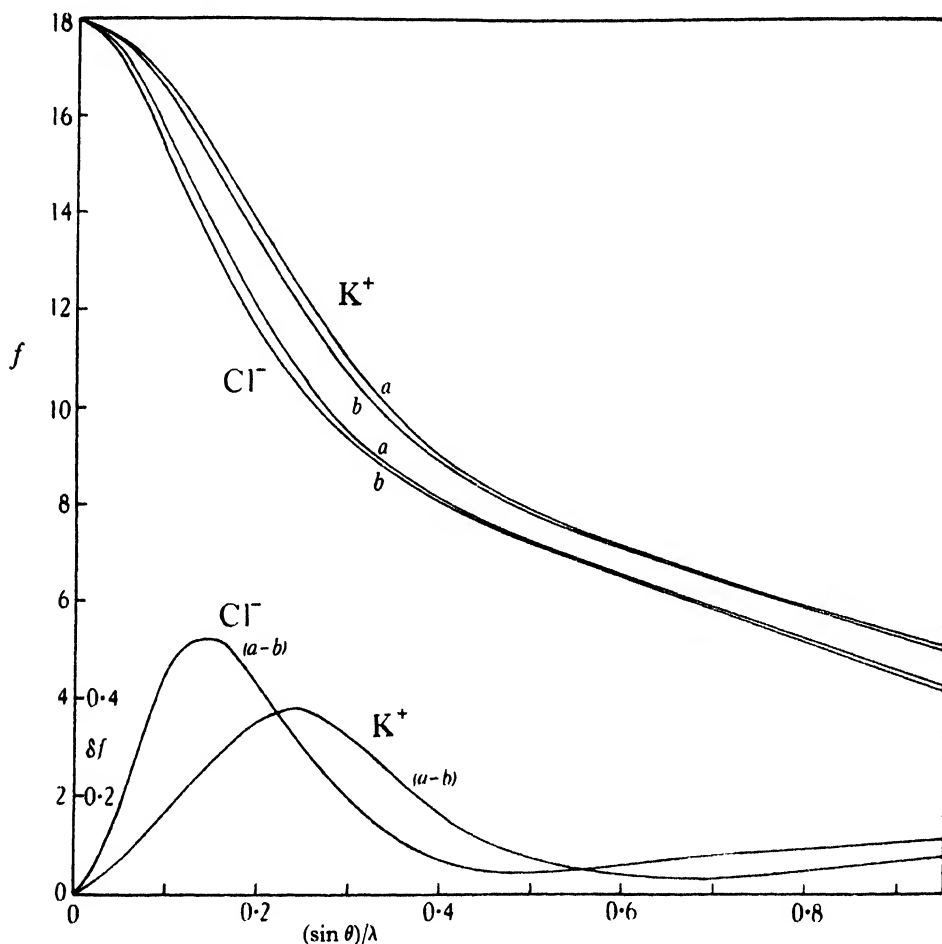


Figure 1. Atomic scattering factors of K^+ and Cl^- with and without allowance for electron-exchange; curves marked *a* are with exchange and curves marked *b* are without exchange. The ordinates of the difference curves, $a-b$, are increased ten times.

§ 6. COMPARISON OF EXPERIMENTAL AND THEORETICAL RESULTS FOR POTASSIUM CHLORIDE

The experimental values of f in the final column of table 2 are compared with the theoretical values in figure 2; the experimental values are shown by circles and the calculated values by full curves, the upper curve being the scattering factor with allowance for electron exchange. The agreement between the observed and calculated values is, on the whole, very close.

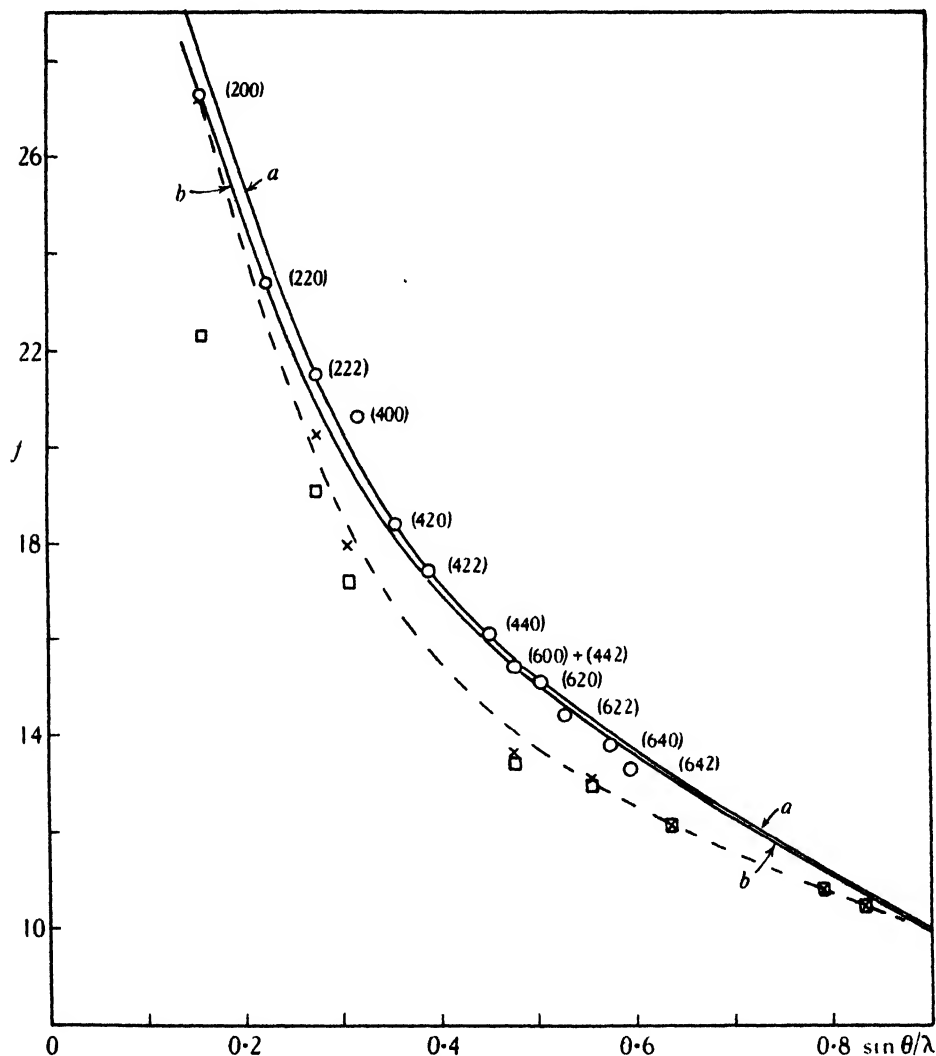


Figure 2. Comparison of experimental and calculated scattering factors for potassium chloride. The upper curve *a* is calculated with and the lower curve *b* without allowance for electron-exchange. Present experimental results are shown by circles; previous measurements by squares and crosses. The dashed curve is a mean curve through the earlier measurements shown by crosses

The previous measurements of James and Brindley⁽¹³⁾ are shown up to a value 0.85 of $(\sin \theta)/\lambda$ by squares and crosses; the squares are the observed values without correction for extinction and the crosses are obtained after correcting for extinction. This correction was made by assuming the *calculated* value for the 200 reflection; the corrections for the other reflections were then obtained by applying a formula due to Darwin. Although the calculated curve with allowance for electron-exchange would give a slightly greater extinction correction, the increase is quite insufficient to account for the discrepancy between the observed and calculated values, particularly between the values 0.4 and 0.7 of $(\sin \theta)/\lambda$. In the region of the value 0.8 of $(\sin \theta)/\lambda$, the measurements are in good agreement with the calculated curves and this agreement holds to much higher values of $(\sin \theta)/\lambda$ than can conveniently be included in figure 2; the highest-order reflection measured was the 16, 0, 0 for which $(\sin \theta)/\lambda = 1.276$. These high-order measurements were made possible by the use of molybdenum K_α radiation and working at liquid air temperature. With copper K_α radiation the highest order which can be accurately measured is the 6, 4, 2; the 8, 0, 0 reflection occurs but is too weak for accurate measurement.

The present measurements show satisfactory agreement with the calculated curves throughout the range in which the discrepancy was previously found. The general run of the points does not fit either curve exactly, although between the values 0.25 and 0.45 of $(\sin \theta)/\lambda$ the observed values fit the upper curve very closely. The higher-order reflections between the values 0.5 and 0.6 of $(\sin \theta)/\lambda$ show a tendency to fall below the calculated curves, but the difference is not large and is within the limits of experimental error.

§ 7. SCATTERING FACTOR FOR COPPER

The charge-distribution of Cu^+ has been calculated with and without allowance for electron-exchange by D. R. and W. Hartree⁽¹⁰⁾ and by D. R. Hartree⁽⁵⁾ respectively. An experimental determination of the scattering factor of metallic copper for copper K_α radiation has been made by Brindley⁽¹⁾, in whose paper references will be found to earlier determinations by Brindley and Spiers, Armstrong, Wyckoff and Rusterholz. The measurements were made by the powder method and standardized with respect to aluminium reflections. Direct comparison between the observed and calculated scattering factors was not possible owing to the large dispersion effect when copper K_α radiation is reflected by copper. It was shown, however, that the difference between the experimental f for copper K_α radiation and the calculated values valid when $\lambda \ll \lambda_K$ gave a mean value 2.6 of Δf , which is in close agreement with theoretically calculated values. It is of interest, therefore, to see what effect allowance for electron-exchange will have on the theoretical values of f . The results are given in table 4.

The experimental values of f_T for copper with copper K_α radiation are given in table 5. The temperature factor, e^M , is calculated from the characteristic temperature, which for copper is 315°K. , by means of the usual Debye-Waller expression. The experimental values of f for copper K_α radiation are given in column 5 of

table 5, and the corresponding theoretical values of f with allowance for electron-exchange and valid when $\lambda \ll \lambda_K$, are given in column 6 of the table; values of the difference, Δf , are given in column 7. The mean value of Δf , $3\cdot0_9$, is larger than the values $2\cdot6$ and $2\cdot3$ obtained theoretically by Hönl⁽¹¹⁾ and by Williams⁽¹⁵⁾ respectively. Since the values of Δf in table 5 are the *differences* between the nearly equal values in columns 5 and 6, it follows that small errors in these values would have a relatively large effect on the Δf values, and in fact errors of the order of 1 per cent in the quantities f_T , e^M and the theoretical f values acting in the same direction would be sufficient to account for the apparently high values found for Δf . The agreement between the Δf values in table 5 and the directly calculated values of Hönl and Williams is probably as good as can reasonably be expected.

Table 4. Calculated scattering factors for Cu^+ with and without allowance for electron-exchange

$(\sin \theta)/\lambda$ (atomic units)	0.0	0.05	0.1	0.15	0.2	0.25	0.3	0.35	0.4
f , with exchange	28.00	26.84	23.95	20.48	17.16	14.40	12.12	10.35	9.08
f , without exchange	28.00	26.58	23.35	19.80	16.49	13.80	11.75	10.20	9.02

Table 5. Comparison of observed and calculated scattering factors for copper

Spectra	$(\sin \theta)/\lambda$	f_T (copper K_α)	e^M	f (copper K_α) measured	f ($\lambda \ll \lambda_K$) calculated	Δf
111	0.241	18.37	1.031	18.94	21.95	3.01
200	0.278	16.58	1.042	17.24	20.60	3.34
220	0.393	12.46	1.086	13.53	16.60	3.07
311	0.461	10.27	1.121	11.52	14.60	3.08
222	0.481	9.51	1.132	10.76	14.08	3.29
331	0.605	6.98	1.218	8.44	11.32	2.88
420	0.621	6.51	1.230	8.00	11.00	3.00
Mean						3.09

§ 8. CONCLUSIONS

In these experiments we have been concerned primarily with tracing the origin of the discrepancies found when the intensities of X-ray reflections from powders are standardized with respect to reflections from aluminium and potassium chloride respectively. It is shown that whereas the scattering factors of aluminium obtained by the powder method agree closely with the single-crystal measurements of James, Brindley and Wood, and with theoretically calculated values, the scattering factors of potassium chloride obtained by the powder method differ from those measured on single crystals by James and Brindley. The difference occurs mainly in the region where the previous measurements showed marked disagreement with the theoretically calculated values; the present values are found to be in good agreement with the theoretical results. The discrepancies found in the powder method when

potassium chloride and aluminium reflections are used as standards have arisen, therefore, through using the single-crystal measurements for potassium chloride as standard values.

The scattering factors of K^+ , Cl^- and Cu^+ have been recalculated from the recent results of D. R. and W. Hartree for the wave functions of these ions obtained by the method of self-consistent fields with allowance for electron-exchange. It is shown that allowance for electron-exchange has only a small effect on the scattering factors, giving slightly higher values.

§ 9. ACKNOWLEDGEMENTS

We wish to thank Prof. Hartree, F.R.S., for kindly allowing us to use the results for K^+ calculated by himself and W. Hartree prior to their publication. We wish to thank also the Government Grants Committee for a grant with which part of the necessary apparatus was purchased, and Prof. Whiddington, F.R.S., for his interest in the work. One of us (P. R.) is also indebted to the Department of Scientific and Industrial Research for a maintenance grant.

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DISCUSSION

R. W. JAMES: The paper appears largely to remove the discrepancies between the theoretical scattering factors for potassium chloride, and those measured by Dr Brindley and myself in 1928. At the date of the earlier experiments it seemed likely that some, if not all, of the lack of agreement would prove to be due to the approximations which had of necessity to be made in calculating the wave functions of K^+ and Cl^- by the method of the self-consistent field. Later work by D. R. Hartree and W. Hartree, in which allowance was made for electron-exchange, has shown that it is improbable that the discrepancies can be accounted for in that way. They are in fact almost certainly due to some systematic error in the earlier observations, probably connected with the use of large crystals as reflectors.

It will be seen that the observed results are always lower than the calculated ones, and the sources of error most likely to arise in the use of large crystals are such as to diminish the reflected intensities. The crystal faces had to be ground and this may have produced a non-crystalline layer which would act simply as an absorbing screen. The crystals of potassium chloride did in fact show a certain toughness and resistance to grinding which led us to suspect at the time the formation of such a layer, and the crystals were etched with water to remove it. This etching did as a rule appreciably increase the intensity, but the trouble may not have been entirely removed. Roughness on the surface, too, might act as a screen to considerable areas of the surface, particularly at oblique incidence. All such sources of error should become less important for the higher-order spectra, and this expectation again is supported by experiment.

It is satisfactory that this new work of Dr Brindley and Mr Ridley shows such good agreement between theory and experiment. The older experiments were done at a time when it was doubtful whether there was any agreement at all between theory and experiment in X-ray scattering. It showed that there was substantial agreement and so served its purpose at the time; but it is natural and satisfactory that improved experimental technique should give more reliable values.

Dr J. C. M. BRENTANO: I fully agree with the point stressed by the authors that the mixed powder method should not be applied indiscriminately to coarse particles. This point is so well established that the results of the experiments might almost have been foreseen, though this in no way detracts from their very great value in drawing attention to its importance in actual practice, when it is but too easily overlooked. The results of our respective experiences differ somewhat regarding the scope which can be given to the substitution method; the authors advocate it as a more general way for obtaining comparative values of scattering factors from coarse powders than appears warranted by our own findings. The point of difference arises essentially from this, that the elimination of the one particular error associated with the use of the mixed-powder method with coarse particles does not preclude a number of other less easily detectable errors associated not only with the numerical values of the absorption coefficients but also with the coarseness of the particles; a detailed investigation seems thus to be required for each individual powder. A fuller discussion is excluded from these comments. Reference may therefore be made to a paper in *Z. f. Phys.* **99**, 65 (1936) and to a joint paper by A. Baxter and myself, *Phil. Mag.* **24**, 473 (1937). These points are discussed in detail in a paper to be published in the next part of these *Proceedings*.

AUTHORS' reply. With regard to the statement that "the results of the experiments might almost have been foreseen", we consider that the question of the effect of coarse particles on intensities measured by the mixture method had not been adequately established, and that the results show what occurs in actual practice. Any theoretical analysis is only possible if very considerable simplification is introduced as to the size, shape and orientation of the particles. With regard to the other points raised by Dr Brentano, we look forward to his forthcoming publication in which he proposes to discuss them more fully.

THE NATURE OF FATIGUE* IN THE AUDITORY SYSTEM

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ABSTRACT. The ear is fatigued by a note of known frequency and known absolute intensity. The decrease in aural sensitiveness caused by exposure to this note is found by making a series of threshold measurements at short consecutive intervals after the cessation of the sound. The note used for threshold measurements is 410 c./sec., while for the fatiguing note both this frequency and others, within a range of 25 c./sec. to either side, are used, at two widely separated levels of intensity. When threshold determinations are made at the frequency of the fatiguing note, the duration of the auditory fatigue increases with the intensity of the fatiguing stimulus to attain rapidly a maximum value. At any frequency below or above that of the fatiguing note, the duration of the fatigue again increases with increase in the intensity of the fatiguing tone, but does so less quickly. The range of frequency over which auditory fatigue is apparent decreases as the intensity of the stimulus decreases. The results are shown to be consistent with the resonance theory of hearing.

§ 1. INTRODUCTION

DURING recent measurements on minimum audibility⁽¹⁾ certain supplementary phenomena were observed which seemed to be attributable to aural fatigue. Reference to literature revealed the paucity of fatigue data; much of the work ignored many necessary psychological conditions or else, satisfying these, failed to furnish sufficient information in regard to the power and purity of the fatiguing source. As an accurate and convenient method for measuring minimum audibility was to hand, the writer extended the method to the investigation of aural fatigue, bearing in mind both the general and particular conditions with which it was essential to comply.

§ 2. OUTLINE OF THE METHOD

The scope of the paper is confined to aural fatigue occasioned by exposing the ear to a pure tone of known intensity, and to the subsequent recovery. The behaviour of the ear was ascertained by measuring its threshold audibility at short intervals, both before and after the period of fatigue.

A possible criticism of the method is that the determinations of the threshold may themselves fatigue the ear, so that for the later values of the threshold there is

* Throughout this paper the word "fatigue" has been used to describe the diminution of auditory sensitiveness which takes place when the ear is exposed to sound. Prof. Hartridge has, however, pointed out in a private communication that the effect is quite possibly not due to fatigue in the strict sense; for instance, it may be due to muscular contraction. The word is therefore used here merely as a convenient label for the effect.

the effect of an additional stimulus to be taken into account. The stimuli used in the threshold determinations are, however, very feeble and of very short duration, and so, as appears from the present work, are unlikely to cause additional fatigue. In further support of this it may be noted that threshold measurements made in quick succession in the absence of a preliminary fatiguing sound were sensibly equal from the beginning; see, for instance, figure 4.

To determine the threshold audibility use was made of a standard source which could be made to furnish sound of known absolute intensity, from zero upwards. To fatigue the ear an independent source, also of known intensity and frequency, was used. It was maintained for a period of 2 min. Four different frequencies of the fatiguing source were employed at two widely separated levels of intensity.

The conditions under which the experiment was performed were such as to eliminate, where possible, causes of distraction, i.e. in regard to the position of the observer and to the manner of signalling his response. Background noise was reduced to a minimum, and in cases where it affected the threshold audibility a correction was applied.

The investigations were carried out with thirteen observers.

§ 3. SOUND SOURCES

(a) *The standard source.* For the measurement of threshold loudness it is necessary to know the sound energy incident on the observer's ear. This was done by providing a standard source with a large baffle, so that radiations occurred as from a point source into a semi-infinite medium. The source used was that suggested by Prof. E. N. da C. Andrade in the *Discussion on Audition* held by the Physical Society in 1931. Air in a tube was maintained in vibration by means of a loud-speaker unit attached to one end: the other end was open and served as the source. The energy output was measured in absolute units, the power of the source being calibrated in terms of the electrical supply. A full account of this source has been given in a separate publication⁽¹⁾.

Throughout these investigations the frequency of the standard source was adjusted to a value of 410 c./sec., and to obviate detuning by temperature-change the tube was maintained at a constant temperature. The tone emitted by the source was practically free from harmonics and its intensity remained constant to within 1 per cent.

(b) *The fatiguing source.* It was not thought necessary to determine the power of the fatiguing source very precisely, for it would appear that its intensity would have to vary very appreciably before affecting the aural fatigue. Thus, an error up to 50 per cent was not considered serious.

The source consisted of a Rice-Kellog moving-coil loud-speaker mounted in the centre of a baffle board of 7-ply wood $3 \times 2\frac{1}{2}$ ft. and was operated by means of a suitable oscillator and amplifier. Its acoustical power was measured by matching its intensity with that of a note at the same frequency emitted by the standard source. A number of readings were taken at different intensities and a calibration

was made in terms of the scale reading of a control potentiometer. After a little practice the desired accuracy was readily obtained.

The Rice-Kellog loud-speaker was finally mounted upon a wooden stand so that its centre was on a level with the observer's head and about 20 cm. from it. A wire framework, carrying a central ring, served as a point of reference for the observer's ear.

The fatiguing source was employed at levels corresponding to powers of 1000 and 3.5×10^6 erg/cm²-sec. The intensity of the sound at the ear was 4×10^{-1} and 14×10^2 erg/cm²-sec. respectively. The latter value is below the threshold of feeling.

§ 4. DISPOSITION OF THE APPARATUS

The distribution of sound-intensity from a point source radiating into the half space is, in general, unknown when the presence of objects distorts the sound-field. In this experiment, where results are of a comparative character, such distortions do not matter provided that they are constant. Of greater consequence is irregular background noise, for this would distract the observer's attention and mask the variations which were being sought in the audibility threshold.

A situation in London was chosen. Measurements were made between the hours of 2 a.m. and 5 a.m. on Sunday mornings. The background noise was slight, and indeed on one occasion the main cause of distraction was the dripping of water from a drain pipe 30 m. distant. The measurements were made above an open courtyard which was surrounded by tall buildings, of which a section is shown in Andrade and Parker's paper⁽¹⁾, figure 13. The fatiguing source was placed edgewise on the parapet and was controlled from the transmitting-room.

It was first necessary to determine the minimum audibility. This was carried out as described in Andrade and Parker's paper. Six or seven readings were usually found to be sufficient. The fatiguing source had then to be switched on for 2 min. One minute before doing so, however, the operator rang the telephone bell once, and this warning enabled the observer to alter his position if he was feeling strained. A few seconds after the fatiguing source had been switched off the second series of minimum-audibility measurements was begun. This series was continued for 12 min. It is to be noted that the observer could see nothing of what was going on in the control room and had only his ear to guide him. It was found to be an advantage if, before making threshold measurements, the observer familiarized himself with the apparatus in the control room and also accustomed himself to recognize the frequency at which the standard source was used.

§ 5. RESULTS

Beginning with the fatiguing source at the low intensity, observations were carried out with three different values of the frequency-difference, i.e. the difference, in cycles per second, which exists between the frequency of the fatiguing source and the test note used for minimum audibility. It was found that (1) the fatigue was

greatest when there was no frequency-difference, and (2) a value for the difference could be found at which there was no fatigue. With the fatiguing source at the high intensity, observations were made with four values of the frequency-difference.

For each setting of the fatiguing source observations were made by two or three observers, each observer taking three sets of readings. In figure 1 is shown the relation that was obtained between the threshold audibility and the time interval from the cessation of the fatiguing stimulus. From this curve may be seen the extent to which an observer's readings are in agreement. From figure 2 may be seen the spread of results among three observers. Both of these curves relate to the same setting of the fatiguing source. In table 1 are tabulated the values from which the curves in figure 1 were drawn. In the first column is given the time that has elapsed

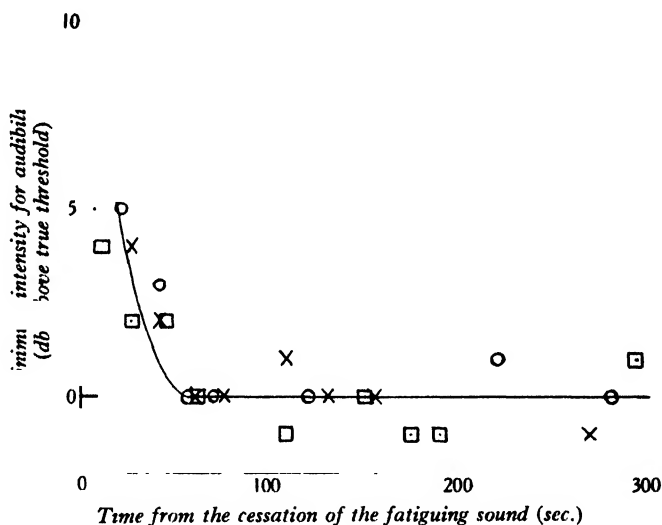


Figure 1. Intensity of fatiguing source, $1000 \text{ erg/cm}^2\text{-sec.}$; frequency of fatiguing source, 410 c./sec. ; r.m.s. pressure-variation at true threshold, 1.30 dyne/cm^2 . Observer A's first □, second ×, and third ○ series of readings.

since the cessation of the fatiguing note, and in the second is shown the incident sound energy in decibels above true threshold. The true threshold was obtained from the minimum-audibility measurements immediately before each fatigue test. Average values for the r.m.s. pressure variations were, for the first three evenings, 1.30 , 0.91 and $1.50 \times 10^{-3} \text{ dyne/cm}^2$, values in good agreement with that previously given⁽¹⁾, i.e. $1.20 \times 10^{-3} \text{ dyne/cm}^2$. On the fourth and subsequent evening a galvanometer of extended range was used and, as this was not calibrated in terms of the former current, absolute threshold values cannot be given.

Figures 1 to 9 are experimental curves relating to the two levels of the fatiguing source and their associated frequency-difference. During the first few seconds the sensitivity of the ear recovers rapidly from a very low value. This initial state of low sensitivity usually lasts less than 20 sec., after which the ear regains, though

more slowly, its initial sensitivity. The time taken for complete recovery is in the neighbourhood of 20 sec.

Table 1. The threshold of audibility subsequent to aural fatigue, for one observer. Frequency of the standard source, 410 c./sec.; frequency of the fatiguing source, 410 c./sec.; intensity of the fatiguing source, 1000 erg/cm²-sec.

Time measured from the cessation of the fatiguing source (sec.)	Threshold of audibility (db. above true threshold)	Time measured from the cessation of the fatiguing source (sec.)	Threshold of audibility (db. above true threshold)	Time measured from the cessation of the fatiguing source (sec.)	Threshold of audibility (db. above true threshold)
20	5	11	8	10	4
40	3	26	4	25	2
56	0	42	2	43	2
70	0	60	0	60	0
120	0	76	0	110	-1
210	1	110	-1	150	0
280	0	132	0	175	-1
—	—	156	0	190	-1
—	—	270	-1	295	1

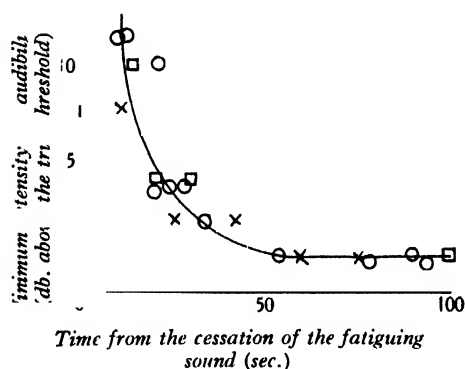


Figure 2. Intensity of the fatiguing source, 1000 erg/cm²-sec.; frequency of the fatiguing source, 410 c./sec.; r.m.s. pressure-variation at true threshold, 1.30 dyne/cm². ○ Observer A; × observer B; □ observer C.

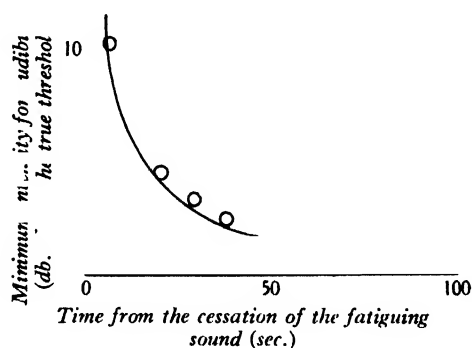


Figure 3. Intensity of the fatiguing source, 1000 erg/cm²-sec.; frequency of the fatiguing source, 415 c./sec.

Consider first the results for the fatiguing stimulus of lower intensity, namely 4×10^{-1} erg/cm²-sec. From figure 2, where the frequency-difference is zero, it may be seen that within approximately 10 sec. the energy required for audibility is only ten times the normal value. When the frequency-difference was increased to five, figure 3, the time required to attain this same value is approximately halved. The sensitivity of the ear is unaffected for the large frequency-difference of 15 c./sec., figure 4.

Figures 5 to 9 indicate the results obtained with the stimulating tone of higher intensity, i.e. 14×10^2 erg/cm²-sec. Comparison between figure 2 and figure 5,

which relate to zero frequency-difference, reveals the surprising fact that between these two cases there is no substantial difference in the nature of the resulting fatigue. When, however, we consider figures 6 and 7, which correspond to frequency-differences of 5 and 15 c./sec., we see that in contradiction to the effect previously noted, the fatigue has not sensibly diminished as compared with the case of zero frequency-difference. A slight diminution is apparent when the difference is 25 c./sec., figure 8.

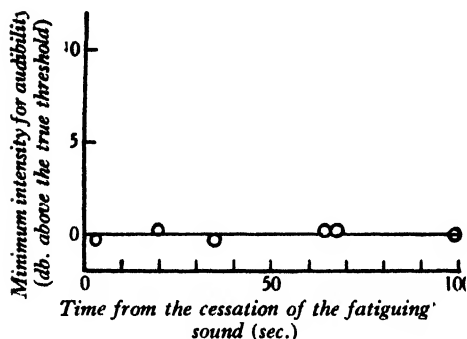


Figure 4. Intensity of the fatiguing source, 1000 erg/cm²-sec.; frequency of the fatiguing source, 425 c./sec.

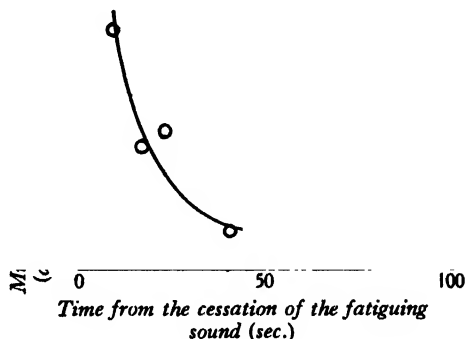


Figure 5. Intensity of the fatiguing source, 3.5×10^6 erg/cm²-sec.; frequency of the fatiguing source, 410 c./sec.; r.m.s. pressure-variation at the true threshold, 0.9 dyne/cm².

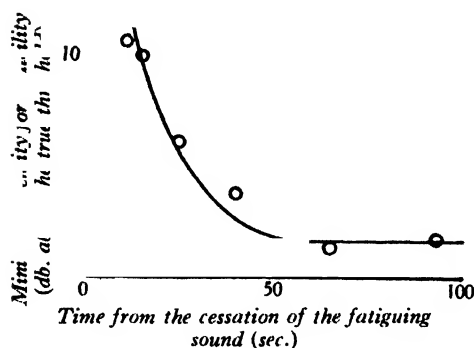


Figure 6. Intensity of the fatiguing source, 3.5×10^6 erg/cm²-sec.; frequency of the fatiguing source, 415 c./sec.; r.m.s. pressure-variation at the true threshold, 1.50 dyne/cm².

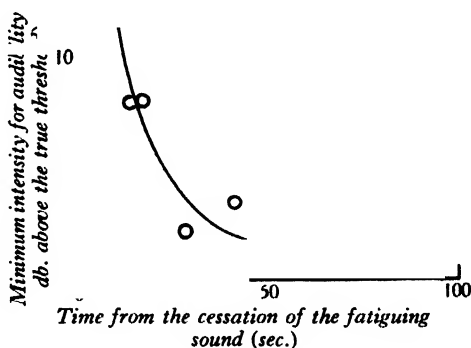


Figure 7. Intensity of the fatiguing source, 3.5×10^6 erg/cm²-sec.; frequency of the fatiguing source, 425 c./sec.

One observer showed in each measurement temporarily enhanced sensitivity, figure 9. His aural sensitivity rose to this level immediately on recovery and persisted for nearly 20 sec. Though measurements were extended over a twelve-minute interval no other observer showed this effect.

§ 6. CONCERNING THE OBSERVERS

The results obtained by the different observers, working without any possibility of being influenced by one another's figures, were found to be in much closer agreement than those generally recorded. Thus, the variation in mean minimum audibility for any particular evening did not exceed 50 per cent.

The thirteen observers who assisted in the measurements were, with one exception, familiar with sound experiments in a physical research laboratory. In addition five were, to a slight extent, musically trained, and consequently they were more capable of differentiating between tones of different frequencies than were the observers who had only an average acquaintance with musical tones. This capacity proved to be of great importance with regard to the reproducibility and reliability of the observer's results. The difficulty experienced by the untrained

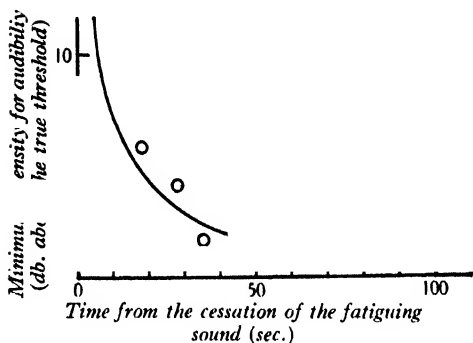


Figure 8. Intensity of the fatiguing source, $3.5 \cdot 10^6$ erg/cm²-sec.; frequency of the fatiguing source, 435 c./sec.

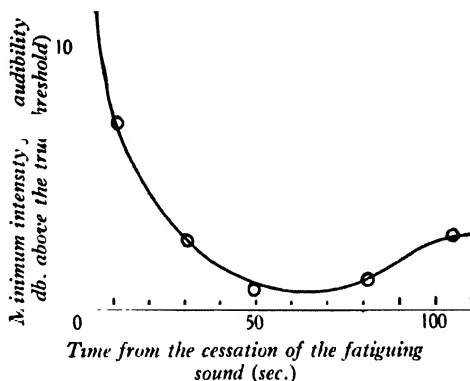


Figure 9. Intensity of the fatiguing source, $3.5 \cdot 10^6$ erg/cm²-sec.; frequency of the source, 435 c./sec.

observer was marked. He was unable to decide, with any degree of certainty, whether the tone was pure or impure, or whether it was too high or too low to be that of the standard source. A feeling of futility then gave rise to a sense of annoyance and exasperation which adversely affected the responses.

The measurements extended over a period of six months and the thirteen observers showed a high degree of consistency. On two mornings the weather interfered with the experiment. On the first occasion the freshening of a light breeze into a gusty wind produced an irregular increase in the general noise-level. On the second occasion the observers suffered such discomfort from cold that they failed to make steady judgements. These two series were abandoned.

A tendency towards false responses, i.e. indications of a threshold measurement in the absence of a sound-field⁽²⁾, was shown by observer B; he was more subject to this tendency during fatigue. The results of an observer's response were not communicated to him, though usually the observer's own judgement regarding his performance was found to be correct; when the results were not satisfactorily consistent he would report, without being asked, that he was not satisfied with his

performance. The majority of observers only responded when aware of a definite aural sensation, but there were four who said that they were aware or sensed the note before hearing it.

§ 7. DISCUSSION OF RESULTS

Aural fatigue was first noticed by Müller⁽³⁾ in 1871 though subsequent experiments, extending to the year 1920, gave little positive evidence as to its nature. An historical survey for the period 1920 to 1927 has been compiled by Pattie⁽⁴⁾, from which it is evident that the data, though more profuse and definite, express markedly divergent views. The first convincing investigations seem to have been made by Yoshii⁽⁵⁾, Wittmaack⁽⁶⁾ and Held and Kleinnecht⁽⁷⁾, who showed, by visual after dissection, that only a limited region of the organ of Corti was affected when the ear was exposed to a pure tone for a sensible interval. It further appeared that whereas this region was confined between narrow limits for tones of low intensity, it became more diffuse as the intensity increased. A similar conclusion has been arrived at more recently by Davis, Laurie, and Stevens⁽⁸⁾. They experimented on guinea-pigs and determined their electrical audiograms over the audible range, both before and after the walls of the cochlea had been pierced to destroy a finite portion of the organ of Corti. When the fatiguing tones were used at a level of 30 db. they noticed that the activated region considerably increased. Dworkin⁽⁹⁾ employed this experimental lesion of the cochlea with cats and concluded against localization of low tones in the apex of the cochlea. It is not clear, from Dworkin's paper, at what levels he used the fatiguing tones or at what frequency.

Neither Wever, Bray, nor Horton^(10,11) were able to detect localization in the inner ear. Horton subjected a number of groups of guinea-pigs to notes at a frequency of 1000, 1500 and 3000 c./sec. for times varying from 100 to 1000 hr. and then tested their hearing by the method of conditioned response. Wever and Bray determined the audiograms of the same animals and concluded, as did Horton, that their aural sensitivity had been impaired more or less over the entire audible range. It is to be noted that the level of their fatiguing tone was 100 db. and this, as the authors themselves suggest, "may involve the entire extent of the basilar membrane and allied structures". Hughson and Thompson⁽¹²⁾ similarly used the Wever-and-Bray technique but found no evidence for localization at low frequencies. Cats were the animals used in this instance. Bast, Eyster⁽¹³⁾ and Culler⁽¹⁴⁾ are representative of those who have extended the Wever-and-Bray technique. They found that localization definitely occurs, though they do not specify which particular part of the ear is involved. Davis and Derbyshire⁽¹⁵⁾ have pursued a more exhaustive study of the Wever-and-Bray phenomena and have differentiated between the action potentials of the auditory nerve and the electrical response from the round window. They have discovered localization of sensitivity within the nerve, a fact which "supports a place-resonance theory of audition". Evidence from a different viewpoint comes from McCrady⁽¹⁶⁾. In a study of the embryological development of the opossum he finds that, according to the human scale, five-sixths of the development in the embryology of the ear occurs after birth. This fact, coupled with a

mammal's instinctive fear of noise, enabled him to record the ear's response along with its development. Notes were employed over the entire audible range and it appeared that whereas high notes were localized in the base of the cochlea, low notes were localized in the apex.

Involved in much of this work is an uncertainty as to which portion of the ear actually constitutes the hearing-mechanism. Guild⁽¹⁷⁾, Bunch and Wolff⁽¹⁸⁾ state that hearing is possible in absence of the organ of Corti. They tested the hearing of a number of patients with various aural conditions and correlated the results with post-mortem microscopical examinations of the ear. In a number of cases in which hearing was good, examination revealed complete atrophy of the organ of Corti. Hughson, Thompson⁽¹²⁾, Bast and Eyster⁽¹³⁾ also conclude that the integrity of the organ of Corti is not essential either for the Wever-Bray phenomena or for hearing.

It should be observed that all of the above instances which refute localization of low tones have involved intense fatiguing tones. Such cases may well be vitiated by reason of the presence of subjective harmonics which, for frequencies below 1000 c./sec., may be as intense as the fundamental.

Experiments of a more physical nature also have produced evidence as to the effect a loud note has upon the ear. Helmholtz⁽¹⁹⁾, as far back as 1885, concluded that fatigue, which results from exposure to pure tones, extends over a finite frequency-difference. He gave the difference as approximately two tones. Measurements made by Flügel⁽²⁰⁾, indicated this difference to be roughly proportional to the minimum perceptible difference in frequency. A more exact measurement by Weinberg and Allen⁽²¹⁾ gave it as 15 c./sec. Evidence for localization is also produced by Fletcher⁽²²⁾ who, when investigating the masking of one tone by another, shows the effect to be localized as regards frequency. Pattie⁽²³⁾, however, concluded that fatigue, induced by a tone of given frequency and intensity, affected the response of all tones subsequently used. He referred to the "non-specificity of fatigue". In general, however, it would seem safe to conclude that exposure to a pure tone fatigues the ear over a finite frequency-difference.

Among physiologists it seems agreed that the activated region of the inner ear increases in extent with increasing intensity of the fatiguing stimulus. Evidence on this point from physical experiments is conflicting. Flügel⁽²⁰⁾ concludes that fatigue resulting from exposure to pure tones is independent of the loudness, while Weinberg and Allen⁽²¹⁾ suggest that fatiguing tones of low intensity may be the more effective in depressing the ear's sensitivity. Unfortunately neither they nor Flügel say how intense were their tones, though it is evident that neither covered an appreciable range. The possibility that an increase in the loudness of the fatiguing tone would cause greater fatigue is given by Pattie⁽²³⁾, who, using a Western Electric Company's audiometer, employed an intensity-range corresponding to 50 and 90 sensation units, the equivalent energy-ratio being approximately 3×10^4 . An investigation along lines similar to those detailed in the present paper has been made by Ewing and Littler⁽²⁴⁾. They found that the intensity level of the fatiguing tone must reach a certain minimum before fatigue occurs. This level was 55 db. at a frequency of 250 c./sec. and 115 db. at 2048 c./sec. They arrived

at no specific conclusion as to the extent of the fatigue, but found considerable differences among different observers. Unfortunately, with two exceptions (namely at 400 and 3000 c./sec.) the threshold values were determined at intervals of one octave, a fact conducive to error by reason of various resonances and subjective harmonics. The threshold note was adjustable in units of 5 db.

The investigation detailed in this paper leads to explicit evidence concerning the nature of auditory fatigue. It is concluded that as the intensity of the fatiguing tone is increased the auditory fatigue becomes apparent over a wider range of frequency. For the two intensities of the fatiguing source used here, the magnitude of the fatigue remained independent of the loudness of the fatiguing source so long as its frequency, and that of the test note, were equal. However, during recent work on minimum audibility, auditory fatigue of a small magnitude was occasioned by tones of very low intensity, namely 2 db. It would thus seem that the magnitude of the fatigue increases with the loudness of the fatiguing tone till it rapidly attains a maximum value, and there remains steady until the threshold of painful loudness is reached. When the frequency of the two sources differ, and the intensity of the fatiguing source is increased, there is no fatigue until the intensity attains a certain minimum value, thereafter the magnitude of the fatigue increases to a maximum value.

These results are interesting in so far as they may be related with existing theories of audition. One or other of two theories, the telephone and the resonance theory, is now generally accepted; their merits have been recently discussed by Kagen⁽²⁵⁾ in accordance with existing data. The theory of resonance, first clearly postulated by Helmholtz, postulates that resonance in the region of the basilar membrane results in stimulation of the nerve terminals over a finite section, the particular part of the membrane involved depending upon the frequency of the stimulus. Wegel and Lane⁽²⁶⁾, in an experiment concerned with the masking of pure tones, obtained a hypothetical curve of vibration for the basilar membrane. This indicates that the extent of the stimulated region increases with the intensity of the stimulus. Now, as only those nerve endings which are stimulated would suffer fatigue, these theories at once suggest that, though localized, auditory fatigue resulting from exposure to a pure tone would increase in extent with increase in the intensity of the stimulus. Further, there would be no fatigue provided that the frequency of the testing note, and the frequency of the stimulating tone, differed by a large interval and was not harmonically related. The results are, then, consistent with the resonance theory of audition. Moreover, the fact that the magnitude of the auditory fatigue increases with the intensity of the fatiguing stimulus up to a certain point, suggests that the mechanism depends in some way upon the amplitude of stimulation of the nerve endings. In particular, there would be a minimum amplitude of motion of the basilar membrane at which full fatigue occurs.

§ 8. ACKNOWLEDGEMENTS

In conclusion I wish to express my indebtedness to Prof. E. N. da C. Andrade, F.R.S., at whose suggestion the investigations were made, for his continued interest and encouragement and for the experimental facilities placed at my disposal. My thanks are also due to Prof. D. M. S. Watson, F.R.S., for placing a room in his department at my disposition, and to the friends who helped me in making the tests.

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THE APPRAISEMENT OF LIGHTING

The twenty-second Guthrie Lecture, delivered on 22 October 1937 by

C. C. PATERSON, O.B.E., D.Sc., M.I.E.E., F.INST.P.

§ 1. HISTORICAL

IN the archives of one of our Ancient City Guilds, the Worshipful Company of Tallow Chandlers, we have an early document of 1680 bearing upon the official appraisement of lighting—in this case the public lighting of the City of London.

It takes but a minute to read a few extracts from this very human document—an appeal to the Court of Common Council of the City of London by the Craft of the Tallow Chandlers. These craftsmen had already for two and a half centuries enjoyed a practical monopoly of the field of artificial lighting, for tallow candles had been the recognized means of artificial lighting with hardly a rival since before the coming of the Conqueror. The makers of tallow candles were suddenly faced with a rival luminant—or as they charmingly called it, *lucidary*—the oil lamp.

This is the substance of their petition:

REASONS humbly offered to the.....Lord Mayor, Aldermen, and Commons of the City of London.....by the Worshipful Company of Tallow Chandlers against Setting up and establishing the Lamplights of any sort in this City, as varying from the antient custom.

THAT this Company have been Incorporated about 230 years..... and have always assisted as well in Purse as Person to add to its Grandure, and to the support of the present Government.

That this Company, with the whole City.....thought themselves safe from any other invasion of their Laws, one of which is an Act of Common Council, made the 3. of October 1599, whereby every Householder from the first of October to the first of March in every year for ever, should cause a substantial Lanthorn and a Candle of Eight in the Pound to be hanged without their Doors.

That notwithstanding the said Act (still in force) certain unfree Men, who are not capable of serving any office in any Company, nor Office of Trust within this City.....have set up, and do continue in the Streets of this City.....a great number of *Convex-Lamps* and other *Lucidaries*, in opposition to, and derogation of, the said Act, and to the manifest Injury of this and other Companies, in their lawful Trades.

That the setting up, and use of the said *Lamps*.....will be a great Prejudice:

First, to this Company, in taking away the Use of their lawful trade....and that if the continuance of these lamps be suffered, they will hinder the making and selling of Seventeen Dozen of Candles to every Lamp set up and used in this City....in every Year....

And although great annual Rents, and other Considerations may be offered to this City by the Partners of the several New Lights, (and as they pretend) towards payment of the Orphans, yet nevertheless it's hoped, that not any of those New Lights will be Established for the sake of such Rents; and at the same time, by so doing, deprive the Tallow-Chandlers, and other Trades in the Profits thereof, to a far greater value than the Profits of the Lamps can accrue unto the Orphans.

And to other Trades, as the Horners in making of Leaves for Lanthorns for burning Candles in; Tinmen and Spinners of Cotton, whereof the Twentieth part is not nor cannot be used in Lamps, which is, and must be in Candles; and must necessarily deprive many Hundreds of Persons, (that live solely by those Trades), of their Maintenance and Livelyhood.

It is humbly hoped that the Act of *Common Council* for enlightening the Streets of this City with Candles in Lanthorns may be strictly observed, or that this Honourable Court will be pleased to make another Act, for the more strict and regular Observance of the Duty of Lighting the Streets of this City.....with Tallow Candles in Lanthorns, which will be cheaper to the Inhabitants than any sort of Lamps.

You will notice that each householder was from 1 October to 1 March in every year *for ever* to cause a substantial lanthorn and a candle of eight to the pound to be hanged without their doors. There is still something to be said for the method these pioneers used for appraising their light. Being at that age uncontaminated by the conceptions of physics, they resisted the temptation to specify *light* and insisted with touching reiteration on the two tangible things they knew—the tallow candle and the lanthorn. This simple and commonsense principle of appraising lighting by boldly specifying the lamps which radiate the light is probably still the most widely used in common practice.

§ 2. OBJECT OF LECTURE

I am apprehensive lest this talk should degenerate into a mere lecture on photometry, and an indifferent one at that. For my object is wider. It is rather to review some of the many and varied circumstances in which one characteristic or another of light must be estimated in relation to the purpose for which the light is required. Nevertheless, the measurement of light by physical or physiological means is in fact the inevitable background of my subject.

The essential motive in the inception of the Physical Society was the study of experimental physical methods. I need make no excuse this evening therefore if I centre my discourse round various techniques which have been evolved by the physicist and the engineer for the better study of the art of using light. The contributions of the physiologist are at least as important. Certain techniques can be considered to be as much within the sphere of one as of the other, but my point of view and terminology will, I admit, not be that of the physiologist, although

I hope that nothing I say will be at variance with a sound physiological standpoint.

When I joined the National Physical Laboratory some 35 years ago with the task of evaluating and rendering as reproducible as possible the unit of luminous intensity, i.e. the candle, few people thought of the value of light to the community in terms of anything but intensity. This was unfortunate, but perhaps natural, because the intensity of a source of light was the one quality which could be readily measured. Furthermore, the idea was simple enough for engineers to understand.

The measurement of brightness, of total flux, of colour, of contrasts, of the disturbing effect of unwanted light, the differences between normal eyes, and such like—measurements of all these quantities had yet to come. Some of the techniques for them are still very imperfect; but realizing the importance of the effects for practical lighting, workers are now having to seek techniques for appraising even the most elusive of them.

In some of these techniques matters have been much complicated by the appearance of new lamps which yield light of the most varied colours. The appraisal of lighting effects was difficult enough when our lamps emitted approximately white light, i.e. light which can be matched in its hue with that from a black body at some temperature or another. But now that so many lamps emit merely a line spectrum of some gas or vapour, our technique must no longer assume (as it used to do) that the light emitted approximates to that of a continuous spectrum.

§ 3. LUMINOUS INTENSITY

(a) *Visual techniques.* In the early years of the century our carbon-filament substandard lamps had hardly been established before the operating temperatures of incandescent lamps began to climb. The Nernst lamp, then Tantalum, Osmium and Tungsten appeared, bringing with them disturbing changes in the hue of the light.

It was fortunate that there were good physicists at that time who foresaw that alongside the effort to evaluate such higher-temperature sources by the old methods of direct photometric comparison, a sounder and more fundamental technique must be established, based on spectrophotometric methods. The Americans undertook several very laborious investigations to determine the relative luminosity curve, figure 1, for the average human eye—the type of curve which was, I believe, first produced by Sir William Abney. From 1912 to 1922 curves were obtained for about 250 observers, and as a result (and also because the results of measurements on a group of Japanese observers showed no sensible racial disagreement, such as was at one time suspected), the average curve, figure 2, was internationally agreed. But it does not do to forget that this average curve has as its origin the diagram shown in figure 1, in which we observe the very great spread which prevails amongst normal individuals.

To allow for the deviation of individuals from the average colour-sensitivity, a system, due to Ives, has been evolved for determining, by a simple test, the extent

of the departures of individual observers from "average vision", so that an appropriate correction can be made to photometric observations in which a colour difference is present. This is a partially successful device only, but on the whole we are better off with than without it. Briefly, the test consists in determining for any observer the ratio of the transmissions of specified yellow and blue filter solutions, with a Guild flicker photometer at a high field brightness, 2.5 equivalent ft. candles,

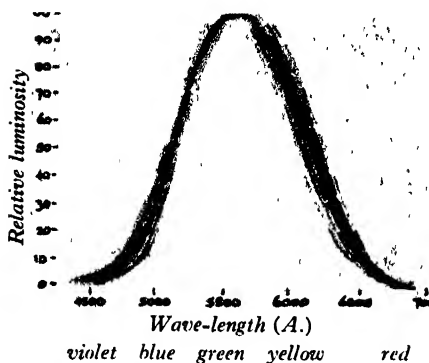


Figure 1. Curves of relative luminosity for 125 persons.

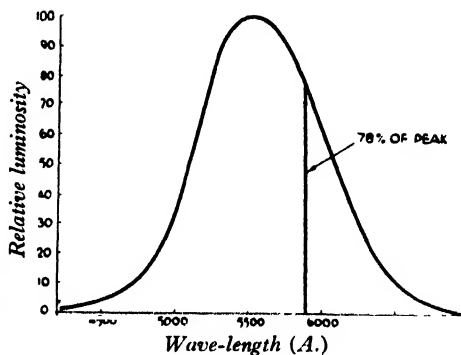


Figure 2. Curve of average relative luminosity, adopted internationally.

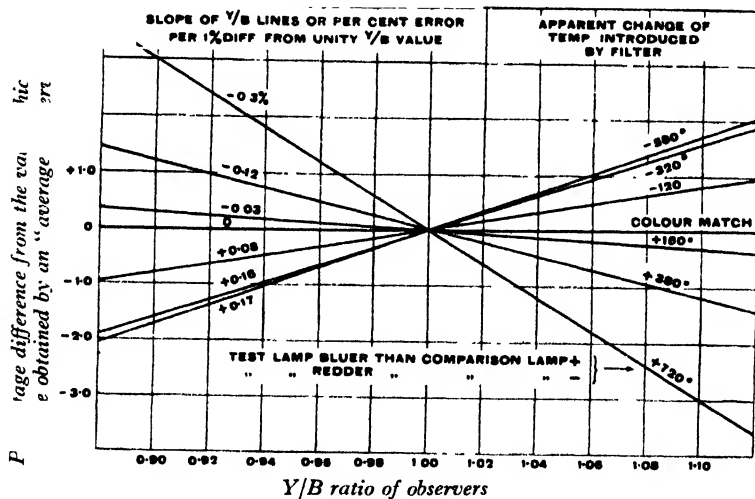


Figure 3. Lines relating Y/B of observers in the comparison of light sources operating at different colour temperatures.

in order to ensure that the test shall apply to foveal vision. Normal observers' yellow/blue ratios range over a spread of about ± 15 per cent from the mean. If these Y/B ratios are plotted against the individual observer's candle-power or lumen determinations in the presence of a colour difference, the slope of the best straight line through the observations is determined by the extent and form of the

colour difference. For example, if we photometer carbon or tungsten filament light sources operating at different colour temperatures, and plot the results against the Y/B s of the observers, we obtain a family of curves having different slopes, figure 3. If we then plot the slopes of these curves against the difference in temperature between the light sources compared, we obtain a straight-line relationship, figure 4, from which we can determine the slope of the Y/B line for any difference of colour-temperatures. Therefore when photometering tungsten or carbon filament lamps, we can, if necessary, make a suitable correction to any individual observer's results provided we know the extent and direction of the colour-temperature difference and the observer's Y/B ratio.

Slope of Y/B line



Figure 4. Relation between slope of Y/B lines and the colour-temperature differences between the sources compared.

This method is only of limited application when continuous-radiation sources are to be compared with sources emitting line or band spectra. This will be appreciated by reference to the diagrams, figure 5, where the results of photometric comparisons between tungsten and neon, sodium, and high-pressure mercury sources have been plotted against the Y/B s of the observers⁽¹⁾ using different forms of photometer head. We see that in some cases the "spread" from the best line through the observations is very great, and in many cases is of the same order of magnitude as the correction which the slope of the line would indicate to be necessary.

It will be seen, therefore, that Ives's proposal is mainly applicable for comparing light sources in which the radiation is continuous and approximates to that of a black body.

Having thus, through the relative-luminosity curve, obtained a value for the luminosity at each wave-length, we can now interpret the spectrophotometric readings on a coloured source of light in terms of the intensity-value of such a source for human vision. It is obvious that the appraisal of light by this technique is easier for radiators with a continuous spectrum than for those with line spectra. The latter cannot in fact readily be measured spectrophotometrically. It is usual in such work to find a colour filter which, when put in front of a tungsten filament

standard lamp of appropriate temperature, will give a colour match (though not an energy match) with the line-spectrum source to be determined. The filter is then measured spectrophotometrically for its absorption, so becoming a standard "colour converter" whose constants are known.

It may be interesting to demonstrate how closely we can approximate, with filters used with filament lamps, to the colour of certain vapour lamps now in common use for public lighting. [To illustrate the description which follows, images of the various photometer fields mentioned were thrown on the screen.]

You will remember how comparatively easy it is to balance a Lummer-Brodhun photometer with a large field (6 to 8 degrees) when there is no colour difference present—as for instance when two tungsten-filament lamps operating at the same

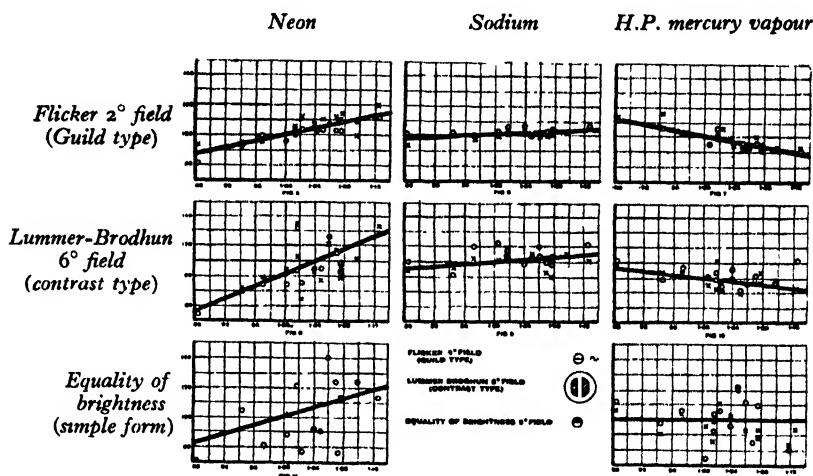
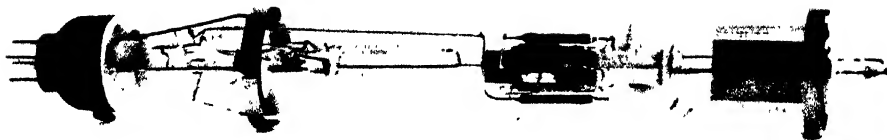


Figure 5. Representative Y/B curves obtained when comparing electric discharge lamps with incandescent tungsten.

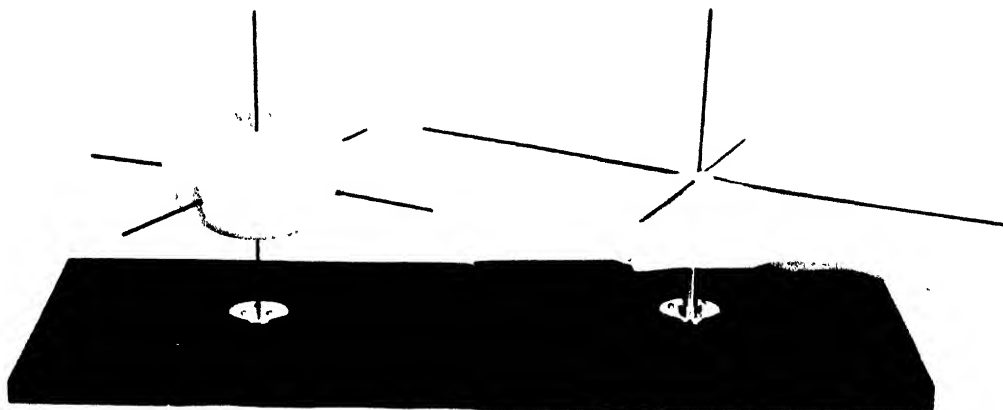
colour temperature are being compared. We will attempt to show, by means of superposed projections, the appearance of different photometer fields when heterochromatic comparisons are being made.

First the 6-degree large Lummer-Brodhun field; we can see, as the brightness of the adjacent fields is adjusted, how difficult it is to balance with the full colour difference between tungsten and high-pressure mercury light. This colour difference can be minimized by means of a suitable blue filter in front of the tungsten source, and you will see now how much easier it is to determine the point of photometric balance as the brightness is adjusted. For the best work a smaller field should be used in order to restrict it to foveal vision. Here is such a small 2-degree equality of brightness photometer with the full colour difference tungsten to high-pressure mercury. And next we see it with the filter in front of the tungsten source to give minimum colour difference.

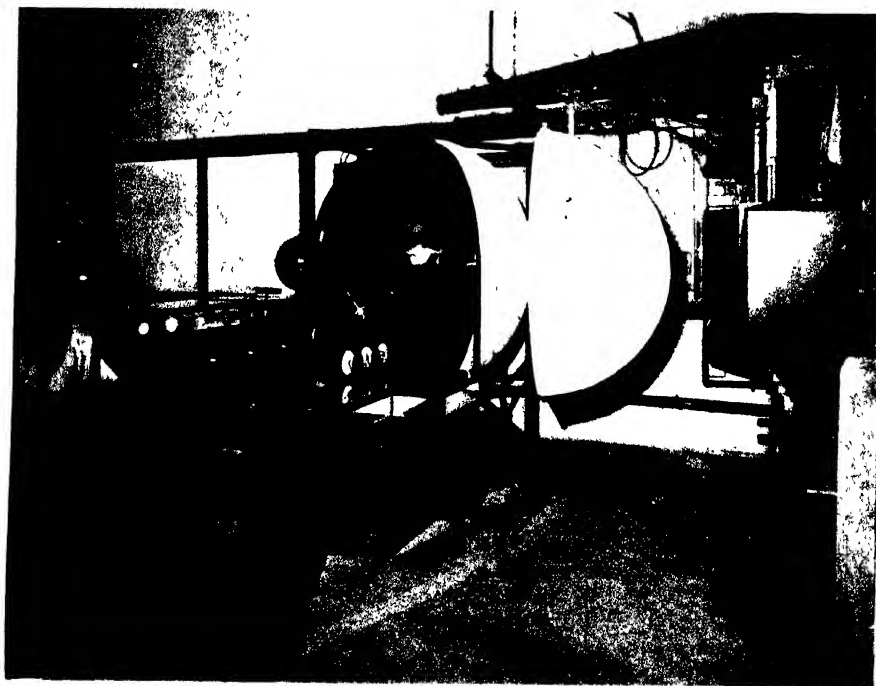
We will now project alternately on to the same portion of the screen, a small circular (2-degree) field from the tungsten and high-pressure mercury sources,



(a) Valve photocell unit.



(b) Models of polar distribution surfaces



(c) Integrating photoelectric photometer for measuring tungsten-filament electric discharge lamps.

respectively. This simulates the conditions in a flicker photometer, such as the Guild photometer, except that in the latter a 25-degree steady white surround field is used to increase the comfort of balancing. The photometric balance in this case is of course indicated by the setting position at which flicker disappears. This we see is fairly easy to determine, even though the full colour difference is present as in this case. Why then use any other photometer than the flicker for heterochromatic comparisons? There is a drawback of course. The flicker photometer must be operated under carefully prescribed conditions and is very tiring to use continuously. It is thus unsuitable for making routine day-to-day measurements. Even with carefully chosen filters and yellow-and-blue-corrected human individuals, the measurement of the intensity of differently coloured modern lamps is liable to considerable uncertainty. So you see it is all rather artificial. We are trying to make of the human eye as accurate and reproducible a measuring-instrument as we can. But when we have done all the things I have just described, I am not sure how justifiable is the claim that we are basing our appraisements of light on the judgements of human vision.

(b) *Photoelectric techniques.* Having consented to this measure of arbitrariness, our critics will hardly complain if we seek the assistance of the photoelectric cell to replace the eye and to relieve it of the tedious and exacting discriminations which this photometric work involves. The photocell of course has its own traps for the unwary, which are both optical and electrical in character. In the case of photocells of the Elster-Geitel type, which are still found to be most suitable for high-precision measurements, the chief electrical uncertainties are surmounted by housing the photocell complete with amplifying valve and grid leak in an evacuated glass envelope, as shown at (a) in plate I. By this means instability due to variable surface leakage is avoided, and the highly insulated lead from photocell to valve is kept extremely short. This enables the unit, together with its associated components, to be efficiently screened from external electrical disturbances.

Other causes of uncertainty in such photoelectric apparatus may arise from (a) the temperature coefficient of the photocell, (b) fatigue, and, in cells of bad quality, (c) departure from linearity of response. Moreover, where it is required to make illumination measurements, errors may occur as a result of departure from true cosine response, and of course from the fidelity with which the relative-luminosity curve of the cell corresponds with that of the average human eye. No cell as yet approaches sufficiently near the required distribution, but Preston at the National Physical Laboratory has studied light-filters for use with a certain thin-film potassium photocell, and has produced the high degree of coincidence shown in figure 6 with a loss of sensitivity of about 75 per cent for tungsten radiation and about 80 per cent for high-pressure mercury lamps. But such a loss does not matter when we can have practically as much amplification as we choose. Thus, you see, by using a photocell with a carefully designed filter and a substandard lamp, we can approximate to the response of the limited region at the centre of the fovea of the average human eye, and so obtain a consistent measure of the intensity of our coloured sources of light.

In general the Elster-Geitel type of photocell is chosen for precision measurements, because of the higher stability available in special types and of the fact that it is a high impedance device and therefore the photoelectric current can readily be amplified. However, the selenium rectifier type of photocell is gaining popularity for industrial photometric purposes because of its simplicity. This type of cell is a low-resistance device which can be connected direct to a low-resistance microammeter of 50 to 100 ohms, the indications of which will be closely proportional to the incident light. Fortunately, the spectral sensitivity of these cells, figure 7, although it departs by an appreciable amount from the "average visibility curve", is a sufficiently close approximation to enable the light-output or illumination from incandescent tungsten sources, over the normal range of operating temperatures,

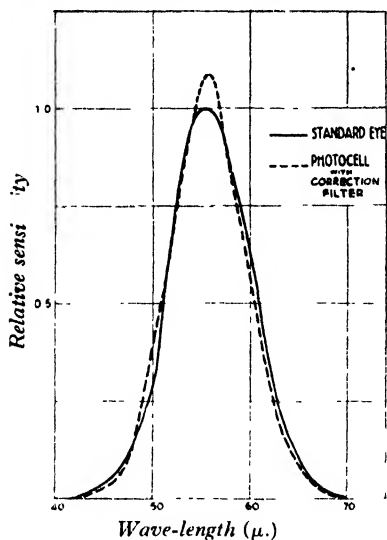


Figure 6. Relative spectral sensitivity of photocell with correction filter to give average-eye response.

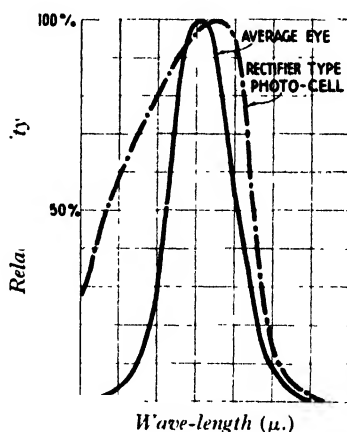


Figure 7. Relative spectral sensitivity of photocell of rectifier type, and of average eye.

to be compared to an accuracy of the order of 5 per cent. Colour filters have also been proposed and made for use with this class of cell so that it may be used for comparing coloured light sources. But the absorption of such filters is necessarily high if accurate correction to "average eye sensitivity" is required, and amplification is not possible owing to the low resistance of the cell, so that the application is strictly limited.

Even though some may be inclined to be critical of all these artificial aids to absolute accuracy, there is no doubt about the extraordinary sensitivity obtainable by the use of the photocell in photometry. I speak of sensitivity, not of absolute accuracy, and for many purposes sensitivity is more important than absolute accuracy.

[The lecturer then showed a photometer and control gear which employs a photocell for appraising the intensity of the light falling on it. The galvanometer was shown to give a deflection of about 3 ft. for a change of $\frac{1}{2}$ per cent in the light

falling on the cell. The apparatus incorporates one of the composite vacuum units referred to earlier in the lecture, the electrical amplifier circuit being effectively screened. Actually the unit used in this photometer is fitted with a grid leak of approximately 10^{11} ohms, giving maximum detectable sensitivity to light of 10^{-9} lumens. This is reduced to 10^{-7} when the apparatus is used with the galvanometer incorporated in the control cabinet.]

The photoelectric photometer is an exceedingly useful technical device and a tribute to those who have brought it to such a state of refinement. But it does not concern us or assist us very much in the broader aspects of the appraisal of lighting.

There is one application which demonstrates very well the convenience of the selenium rectifier photocell in an industrial laboratory. Polar curves of lighting fittings—or may we call them “lucidaries”?—are tedious to take and to plot. This is particularly so with many modern types of which the polar curve is not a figure of rotation but is designed to be asymmetric, in order, for instance, to throw more

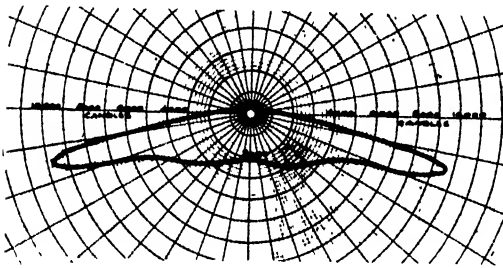


Figure 8. Polar distribution curve of asymmetric refracting lighting fitting.

light up and down a street than across it, figure 8. In order to define them, such lucidaries require a considerable number of polar curves taken in different planes through their vertical axes, which is all exceedingly tedious. Two solid polar graphs are shown at (b); plate I

[A device was then demonstrated in which a photocell rapidly explores and records the light-intensity in one plane after another, enabling the work to be done expeditiously. The only skill required is that of the operator who must faithfully follow the vagaries of the track of the spot of light on the polar chart.]

There is now a high probability that the accepted standard of luminous intensity will no longer, as heretofore, be a pentane lamp nor a Hefner lamp, nor tungsten lamps calibrated in terms of these, nor even, as defined by Act of Parliament, a “sperm candle weighing 8 to the pound”. But that one square centimetre of black body at the freezing point of platinum will be assigned the value of exactly 60 candles. Such a standard, though arbitrary, leaves the value of our present unit practically unaltered, and will always be reproducible. It has in fact been already reproduced within an accuracy of approximately 0.2 per cent at the Bureau of Standards, Washington, and at the National Physical Laboratory, averages of series of some 30 sets of determinations being used.

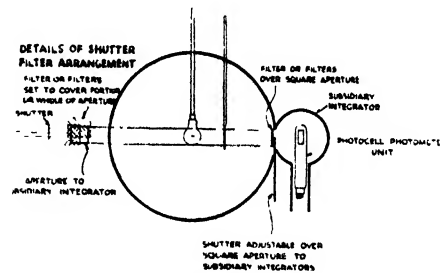


Figure 9. Diagrammatic arrangement of integrators of photoelectric photometer.

(c) *Total flux.* Before we pass from the measurement of intensity we ought to note the technique for obtaining a measure of the total flux of light from a source, or in other words its average intensity. The principle of the Ulbricht sphere is simple and attractive, but it is anything but simple to ensure that the magnitude of the unit of intensity of a standard in a single direction is accurately reproduced in the mean intensity in all directions of any given source. A diffusing, truly white surface is required. It is easy to measure the mean intensity of a source in all directions and make a standard of it for calibrating the Ulbricht sphere. But unless the light from the source ultimately to be measured has exactly the same hue as the light from the standard, errors may creep in. These errors can be of the order of 1 to 2 per cent, with line sources, even when using the accepted white paints available for coating the sphere interiors.

If a photocell is used as a detector with an Ulbricht sphere, it may sometimes conveniently be placed in a subsidiary integrator, figure 11. The window between the main and the subsidiary integrators is occupied by a shutter and appropriate colour filters which adjust the sensitivity and the spectral response of the photocell unit; and as, furthermore, when filters are used in this way, the photocell receives integrated light, the arrangement avoids any inaccuracy, due to variations over the surface of the cell. An integrating photoelectric photometer incorporating this principle and suitable for measuring tungsten filament and electric discharge lamps⁽²⁾ is shown at (c) in plate I.

§ 4. GLARE

Glare. Now these elaborate techniques which we have been reviewing, and all the other refinements which on account of time I have not been able to touch upon, concern merely the appraisal of intensity. But the appraisal of light for seeing purposes depends but remotely on the intensity of sources of light. In fact I think we must agree that to the ordinary man, in his seeing processes, intensity is really but an abstract magnitude, except in one respect: the disturbance of vision owing to the presence of bright sources of light is due primarily to the intensity of such sources. From this point of view, therefore, intensity may perhaps remain of importance as a practical magnitude. This phenomenon of glare has been investigated very carefully during the past few years^(3,4). Glare is encountered in one of its most exaggerated forms in our roads at night, where the two classes of glare are well exemplified. The first is disability glare illustrated by the motor headlight; here vision of objects is to a large extent paralysed by the glaring effect of such lights. The second is discomfort glare illustrated by street-lighting lamps which appear to be close to the objects that one desires to see. Such street lamps are sometimes bright enough in relation to their surroundings to cause a certain measure of disability glare; that is to say visibility is actually improved if the eyes are shaded from the direct light of the lamps. But Stiles's results show that as a rule these street lamps which appear in the field of view do not embarrass the eye in its discrimination of objects; their deleterious effect is limited to causing a sense of discomfort. This probably depends on the

intensity and brightness of the source, the nearness of its image on the retina to the fovea, and the darkness of the background of the general field of view in which such lights are located. I find there is a good deal of confusion of thought on this subject owing to a tendency to jump to the conclusion that when someone is conscious of discomfort glare, visibility is necessarily impaired. I have noticed, furthermore, a considerable difference in the sensitivity of individuals to discomfort glare.

Stiles has shown how the disability effect of glare for any set of conditions can be calculated from laboratory data, and has established much of the mechanism of disability glare; but in some problems practical conditions are so complex as to make the calculation uncertain and tedious, and in some points the gap between laboratory and practical conditions has yet to be bridged. For example, when your field of view, instead of being a uniformly bright area as in laboratory work, is an area of very varying brightness, and glare sources are scattered in it in positions which depend upon the layout of a considerable length of road, it is obvious that the collection of the essential data alone is a considerable task, and their interpretation is by no means either simple or certain. The very nature of the problem has made difficult the construction of a simple field instrument for measuring glare directly which is suitable for engineers to use, although one very ingenious field instrument was made and tried. We have also no way as yet of measuring discomfort glare, and in fact we know little about it. One hopes that some work will soon be commenced on this side of the problem.

§ 5. IMPORTANCE OF BRIGHTNESS AND CONTRASTS

That derivative of intensity, illumination, is slightly more useful as a conception than intensity itself, and also as a practical magnitude, but it is not by illumination that one sees. Illumination is a useful magnitude to the engineer or the architect who, like our tallow chandlers of old, chose to start the problem of seeing properly by providing sources of light. This has been certainly the easiest and most remunerative way to go about the business, but have its consequences always been favourable?

Suppose the craft of surgeons, represented in those days by the Worshipful Company of Barbers, had been powerful as well as enlightened physiologists. And suppose they had said: "This effort of the tallow chandlers to produce good seeing by providing candles is physiologically wrong and incidentally dangerous from the point of view of fire to our city. Man sees by contrast, and contrast alone, and contrast is produced by differences in brightness or in colour between an object and its background, or between the parts of an object. It is true you may sometimes have to assist matters by providing a little artificial light, but study to make your contrasts the best possible for seeing. Our clothing, our articles of furniture, the walls of our houses, the colour of our materials for surfacing pathways, all these factors which help to make things visible to the eye are being left to chance. They must in future be attended to. We will find out how the various contrasts make things visible, attract attention, and please the aesthetic sense, and study the colour and reflection factors of the paints and materials you use, and we will lay down

standards. We will petition for a charter to give us the powers to enforce such standards." Is such an idea so far fetched as it may appear to some of us to-day? After all, it is not difficult to imagine a world in which artificial light-sources were non-existent and in which man had to manage to see by the light of nature, whatever that might be at the time, and by the artificial enhancement of contrasts. The lamp-maker as we know him to-day would of course not exist, and the world would be the poorer by the loss of a magnificent race of men. But would not their place be taken by an enormous industry supported by a century of painstaking research on the way in which we see—on paints, on colour combinations, and perhaps on luminescent materials?

There are of course examples of this sort of approach to be found in some special cases. Thus, where we want to make something particularly visible, such as a buoy at sea or a Belisha beacon or a survey pole on land, we so colour them as to produce arresting and hard contrasts with their backgrounds. Cricket screens and the white boards placed behind railway semaphore signals are other examples. And when we want something to be particularly invisible we copy the insects and birds, who knew all this long ago, and so colour it as to make its contrasts disappear and its outlines break up.

In any case a few centuries of postponement of the coming of artificial light sources, when the standards and magnitudes for appraising light could have been based on what one sees rather than on the operation of lighting, might have done wonderful things in keeping our sense of values right, and it might have produced a world of human surroundings much brighter and better than the one we know to-day.

There are not a few who to-day are restive under the tyranny of the candle and the foot-candle. Dr Luckiesh of the U.S.A. has tried in his writings to urge the engineer to appreciate the essentials of what he calls "the science of seeing". There is, for instance, the school of street lighting engineers and physicists who, because conditions for seeing are usually so difficult in street lighting, have had to study the essentials for good seeing under these exacting, though specialized, conditions. This has compelled them to ignore to a large extent the traditional fundamentals of illuminating engineering, and to seek a more rational basis for their appraisal of lighting.

I do not want to appear altogether to condemn the use of illumination as a gauge for lighting, provided it is not employed as a criterion for situations where it is of little use. For instance, Mr W. J. Jones has recently organized a most extensive and interesting survey of the illumination desired by ordinary people in the simple operation of reading a newspaper. Here illumination is clearly as effective a measure as brightness itself, because in such a test, with the black-on-white contrast of newsprint, the illumination is a sufficiently accurate gauge of the brightness. He obtains, for eyes adapted to a moderate brightness, a distribution curve for tests on 20,000 subjects, figure 10, showing that people on the whole prefer brightness produced by an illumination of 100 foot-candles on a surface which has a reflection coefficient of about 0.4. In other words, it has a brightness of 40 equivalent foot-candles. This value of brightness is in a sense surprisingly high, for the figure to

which we are accustomed to in our homes or offices by artificial light is only of the order of 5 equivalent foot-candles, and in our offices by daylight from 20 to 100 foot-candles.

§6. MEASUREMENT OF BRIGHTNESS: INSTRUMENTAL

Where do we stand to-day in the technique of brightness measurement and in the expression of contrast for seeing? I am afraid we are not very far on when one remembers that colour contrasts as well as brightness contrasts enter into the problem.

The natural method of expressing brightness is of course in terms of intensity per unit area of the surface from which the light comes. Unless, however, the surface is very bright it is most inconvenient to measure directly intensity per unit area. Instrumentally it is more convenient to compare the brightness of the surface in question with that of another known surface illuminated to such an extent that the two surfaces match each other in brightness. The illumination of the known surface is thus a measure of the unknown brightness. In this way we eliminate the necessity of measuring areas, and can express the result in terms of foot-candles of illumination on a perfectly white surface. For simplicity rather than lucidity this latter unit of brightness has come to be termed the "equivalent foot-candle", or "foot-lambert". I am not proud of this term, but no one has found one which is more suitable and it is constantly employed for every-day work and translated into candles per square foot by dividing the equivalent foot-candles, as measured, by π .

My only reason for dwelling on this is that nearly all the measuring devices used for brightness are similar in principle to illumination photometers. In fact every visual photometer is a brightness photometer. When we wish to measure intensity, illumination or flux, we so arrange the instrument that a brightness is produced which is proportional to the quantity concerned. The surface whose brightness is to be measured is viewed in juxtaposition to a white surface of known adjustable brightness.

Photometers intended for measuring illumination by viewing the brightness of an illuminated test surface can also be used to measure other brightnesses, but in general, photometers intended for measuring brightness must be specially designed with very small external fields, for the vision of objects largely depends on brightnesses which subtend very small angles, and the detail of brightness distribution is very important.

Although it is true that the eye is a very bad photometer from the point of view of its absolute response, as a relative brightness photometer it beats most of our instruments in reliability and sensitiveness.

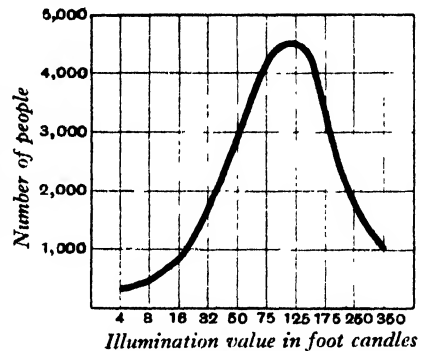


Figure 10. Frequency-distribution curve of values of illumination chosen by 21,179 persons for reading a daily newspaper.

There are one or two simple rough and ready portable types of brightness meter, figure 11, whose accuracy may be put at ± 20 to 30 per cent.

Then there are optical brightness meters or telephotometers, figure 12, which are of two main types, the Maxwellian view type and the telescope type. In the Maxwellian type a lens system focuses an image of distant brightness on the pupil of the eye. The eye then sees the lens flashed with the brightness of the distant object and the lens becomes one of the two comparison surfaces of a photometer system. This type gives a large and conventional photometer field and measures

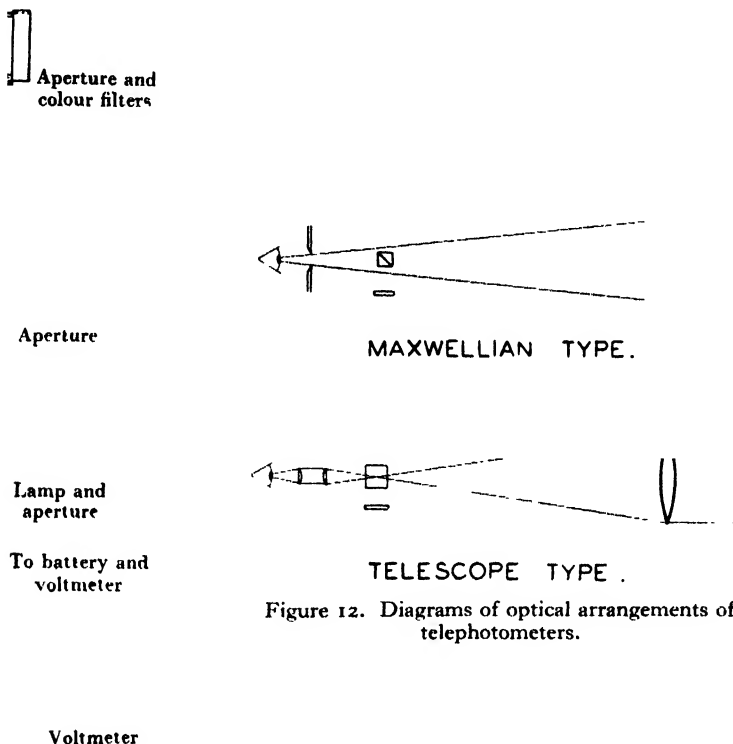


Figure 12. Diagrams of optical arrangements of telephotometers.

Figure 11. Diagrammatic arrangement of a brightness meter.

the average brightness over a small angle. It is not, therefore, disturbed by any non-uniformity of object-brightness, but for small external fields it becomes unwieldy and costly, and there is difficulty in defining the object viewed. In the telescope type of brightness-measurer a small photometer field is inserted into the field of view of a telescope and its brightness is compared directly with that of the image of the distant object. The eye sees the telescope image with the photometer field superimposed. This type permits of the measurement of very small objects and the exploration of the detail. It is small and cheap and there is no doubt as to the object being viewed. It has the disadvantage of being difficult to use at low levels of brightness or with marked colour differences. A small telephotometer



Figure 13. Photographic true-representation negative used in studying brightness under street conditions of lighting.

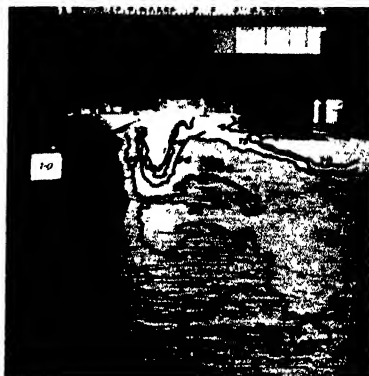


Figure 14. Positive of figure 13 with brightness contours added.



(a)



(b)

Figure 15. (a) contour of equal brightness obtained with contouring densitometer, (b) contour of equal brightness indicated by high-contrast photographic method.

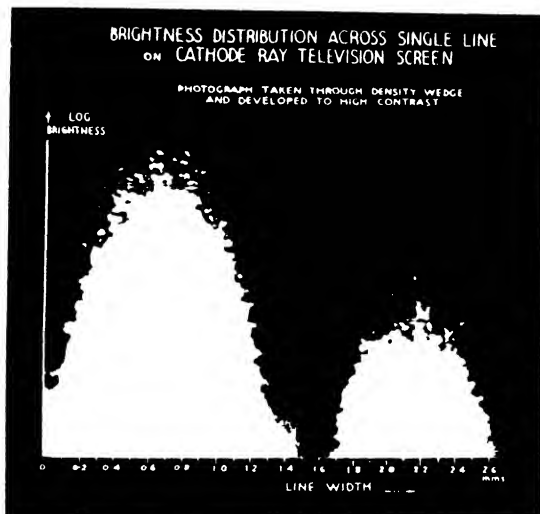


Figure 16. Brightness-distribution across single line on cathode-ray television screen at two different brightness-levels obtained by high-contrast photographic method.



(a)



(b)

Figure 17. Faithful (right) and flattering (left) representation of street lighting.

with a telescope multiplication of 10 can give a field as small as 3 minutes of arc. With a large telescope smaller fields could be used.

These photometers, if used for brightness survey, both involve some system of angular measure in addition to the photometer proper for determining the direction of view. Their accuracy under favourable conditions and when colour differences are not present may be of the order of ± 5 per cent.

§ 7. USE OF PHOTOGRAPHY IN BRIGHTNESS AND BRIGHTNESS CONTRAST MEASUREMENTS

Recently another way of appraising brightness has become more extensively used for many new problems. In this the photographic plate is used in an intermediate stage between the eye and the brightness to be measured. The photographic emulsion has some characteristics very much like those of the eye, both in kind and in degree. The eye has, among others, two sensitivities which we may call the photometric and the geometric; its sensitivity to the amount of light and its sensitivity to the direction of light. The first is a very variable and uncertain sensitivity and, as we have seen, we only use it as a test of equality, not in any absolute way. The second sensitivity, however, is very much more precise, and enables us to detect really extraordinarily fine detail in the objects we see.

The photographic plate is similar. It has a photometric sensitivity (by which it becomes blacker as it is exposed more) which is a rather variable quantity dependent upon many factors, and a geometric sensitivity or resolving power which is very much more precise. Once its vagaries are understood it can, by suitable technique, be used in a great variety of ways for the appraisal of light. Almost always it is used as an intermediary between the object to be appraised and the eye. The photographic plate can record not only the amount of light, but its position or direction; it can record a whole distribution at once, and it retains a permanent record for future photometry if necessary, and has several other unique advantages. For years, of course, it has been used in quantitative spectroscopy, and the way in which quantitative estimates of extremely minute amounts of material can be made through photography will be familiar to all physicists.

Generally, two methods of photographic photometry are possible. The first uses the amount of blackening of a plate to measure the light falling on it. If we use the plate to compare a series of unknown brightnesses with a series of known brightnesses, by comparing the densities of their images, fairly accurate results are possible. The method has, for example, been developed and extensively used for studying brightness under street lighting conditions, for which it is particularly suitable. Figure 13 shows such a photographic negative with its area of unknown brightness and with its known calibration brightness. We can plot out the brightness contours on a positive, figure 14, of the negative by means of the contouring densitometer. In this way the whole field of background brightness can be explored as well as, if necessary, that of objects seen against the background.

Sometimes the photographic emulsion is used in another way. There is a certain low exposure on the plate, below which nothing is recorded, and another high value

above which no further increase of density occurs. If we use a very contrasty emulsion to take a photograph of non-uniform brightness, and print on to very contrasty paper, we can sometimes make the photograph show one contour of brightness without using any densitometer at all, figure 15. Here at (a) is one contour of a single bright area on a road surface from one light source. At (b) is a contrasty print from such an emulsion, showing how definitely and faithfully such a contour can be obtained. In figure 16 we have the distribution of brightness across the scanned line on the cathode-ray tube of a television receiver, at two difference brightness levels.

Another method of photographic photometry has been used by astronomers for years for determining the magnitude of stars. It depends on the fact that, owing to the nature of the light, imperfections in the object glass, unsteadiness of the air, and photographic spreading, the size of the image will vary with the brightness of the star according to the following empirical relationship

$$M = m - k/d,$$

where d is the diameter of the star image, m is the limiting magnitude of the photograph, k is a constant determined from known magnitudes on the plate, and M is the magnitude of the star as determined from the measured diameter d . The constants are determined from a sequence of known magnitudes determined by various methods, one of these being a coarse wire diffraction grating which when placed over the object glass produces images in the several orders, the ratio of the light in these being of calculable amount.

Still a further development, which is not a photometric method but is most useful in the appraisal of light, is the use of accurate photographic records—accurate in the sense that they convey, with sufficient precision for many purposes, the same impression to an observer as did the original scene. This again has been used as a technique for study of street lighting problems, and is a useful tool which can be used in parallel with the methods of photographic photometry to examine the characteristics of satisfactory and unsatisfactory distributions of brightness.

Here are two photographs* of the same street, figure 17. In one of them the artist has used all his craft to make the picture as flattering as possible. It gives us a picture which has little resemblance to the truth, and merely appears to be a temptation to the salesman of street-lighting fittings. In the other the tone values have been determined from a knowledge of the values of brightness existing in the street and of the properties of the eye, so that the photograph conveys, under the conditions in which it is viewed, the most accurate impression possible of the original installation^(5,6). Now that there is this quantitative way of securing correct tone values there would seem to be no excuse for many of the distorted photographs one is so often shown of lighting installations. In spite of its great advantages for some purposes, the photographic method makes great demands on the skill and patience of the experimenter; it is complicated, expensive, and comparatively

* The lantern slides used to illustrate the lecture had regard to the properties of the projection lantern and the conditions of the theatre, the half tone illustrations in this paper are subject to limitations and do not faithfully reproduce the original prints.

inaccurate; nevertheless it has rendered possible many investigations which can be carried out in no other way.

§ 8. PHOTOELECTRIC BRIGHTNESS-MEASUREMENTS

Photoelectric brightness photometry is generally very difficult. The cell is essentially a device for measuring illumination, and has a comparatively large light-sensitive surface. In many brightness-measurements the angle of subtense of the object is very small, so that the flux available is excessively small, and consequently, both in order to collect sufficient flux and in order to keep the external field small, very large optical components would be required. For example, it has been possible to use this method for exploring the brightness distribution across a scanning line on cathode-ray tubes used in television, figure 18. In this case a fine slit is arranged to traverse a ten-times-enlarged image of the line, and a large-aperture short-focus (condenser) lens behind the slit condenses the light down on to the photocell cathode. This method is only made possible by means of the highly sensitive photoelectric photometer referred to earlier. Clearly this type of apparatus is too cumbersome for most types of brightness-measurement, but it is extremely useful for specialized applications.

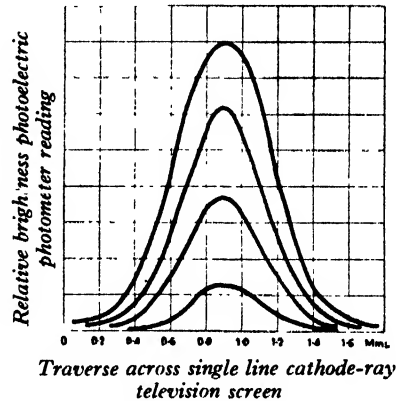


Figure 18. Distribution of brightness across single line on cathode-ray television screen, obtained with photoelectric brightness photometer.

§ 9. APPRAISEMENT OF CONTRASTS

I have already indicated that the chief aim in measuring brightnesses is to facilitate estimation of the contrasts by which we see objects. But there is the obvious objection in this that, whilst brightness contrasts may be measured, if there is a difference of colour the measurements have a very limited meaning. That is where our technique of measurement is so lamentably behind practical needs. Little has been done for directly appraising contrasts even when there is no colour difference. All we do is to measure the brightnesses of the two contrasted surfaces. And even when we have done so there is no accepted method of expressing them in terms of their ability to cause the eye to see them and the brain to appreciate them. I know we have the historic measurements of Fechner's fraction, which gives us the relative brightness difference which we just cannot see in terms of the background brightness. But these results do not help us to assess practical contrasts which are greater than the threshold. We know the percentage contrast which is just seeable, but seldom is it in threshold values that we are interested. The contrasts in the fields we look at are usually well above the threshold; they must be, if seeing is to be tolerable. An overcast day brings nearer to the threshold many contrasts which on a sunny day stand out clearly. But a fuller attention to the subject by the pioneers might

have evolved in some cases sunlight contrasts with overcast skies. The architects of course have done much down the centuries to apply the principles of contrast to building facades. They had to, for they had no aids to lighting externally.

And when we come to colour contrasts our ideas are limited to certain qualitative impressions. We say that yellow is a good contrasting colour, and we probably have opinions on other colours or shades. But a technique is needed for appraising such contrasts other than on the threshold.

Recently the development of the television art has brought a new set of workers with some new techniques into the field of study of picture contrasts. This field has so far been mainly exploited by those interested in the photographic art. The work has been of high scientific merit, and the nomenclature chiefly in terms of emulsion densities and photographic results, but the television process gives an opportunity of controlling contrasts which has not hitherto been possible; for the details of the original picture as well as the details of the reproduced picture are both, at one stage, held in terms of electrical energy and can thus be manipulated—must in fact be manipulated—to give the most effective result. I cannot but believe that continuation of the effort, which television has started, to study the reproduction of scenes for the satisfaction of viewers will carry a stage further the appreciation of the principles of good seeing of pictures, of which the cinematograph industry has laid the foundation.

From a recent paper⁽⁷⁾ on television images, it appears that the range of brightnesses in any picture used at present in television vary from about 15/1 to 120/1, while those used in cinemas vary from about 25/1 to 80/1. The television controls enable the contrast and brightness-range to be varied at will as the picture is viewed—a technique hitherto not easily achieved. It is possible to give an indication of the effect of changing contrasts by superposing two similar pictures, one very contrasty and the other very flat. The extent of the contribution of each picture to the combined picture is varied by means of a neutral absorbing wedge in front of each picture. Thus, within these limits, any degree of contrast is obtainable. Furthermore, any value of average field brightness is secured by increasing or decreasing the intensity on the projector lamps.

It is of particular interest to note the effect of changing contrasts when the average brightness of the picture is low. When the contrasts are made greater, although the maximum brightness is unchanged, we can note how much better is the seeing.

[A flat picture at a low value of brightness was shown on the screen, then the same picture with the same maximum brightness but with the contrasts increased.]

§ 10. APPRAISEMENT OF COLOURED LIGHT

In connexion with the use of gaseous and vapour light-sources for exterior lighting, there is a good deal of discussion and experiment directed to show whether or not it is easier to see in the yellow light of sodium lamps than in that of the less monochromatic sources. Dr Luckiesh has made a good effort to appraise sodium light under the categories of visual acuity, type-reading test, speed of seeing, and

accentuation or otherwise of contrasts. He comes to the conclusion that on balance sodium has no practical advantage over other sources of light. Others contend, mainly on the basis of visual acuity, that it has an advantage, forgetting, I think, that the seeing of fine detail is not usually the chief desideratum in exterior lighting.

We can perceive how much we are at sea in appraising the practical value of the various coloured light sources by lighting some not unusual colours alternately with sodium light and with a light covering the whole spectrum. When this is done we can see how these contrasts, which are clearly marked under normal light, completely disappear or are reversed under sodium light.

By examining between 500 and 600 contrasts it has been found that contrasts which are already marked tend on the whole to be more so under sodium light, whilst those which are normally less well marked tend to be still less so with sodium light. I am calling attention in this way to the importance of colour contrasts with a view to showing how helpful it will be when principles for appraising them or techniques for studying them are better established.

There is such an immediate and pressing demand for simple techniques for measuring and specifying both the *colour* and the *colour rendering properties* of light sources, that we are likely to see a number of new proposals put forward in the near future.

In a desire to remain loyal to the internationally agreed trichromatic system, we should naturally turn to this system for a solution to our problems, but certain practical difficulties arise: Firstly whilst the *colour* of the light can readily be specified on the I.C.I. trichromatic system, the types of visual colorimeter obtainable on which such measurements can be made are unsuitable for making rapid routine determinations, as they require skilled observers to operate them.

A much simpler and more rapid technique for indicating the colour of a light source directly on the trichromatic system has recently been evolved;⁽⁸⁾ this consists of three rectifier type photocells covered with suitable colour filters and connected respectively to three galvanometers. By an appropriate optical system the galvanometers project line images so arranged that, with the galvanometer at zero, these line images form an equilateral triangle. The light which is to be analysed for colour, falling uniformly on the three photocell components causes deflections of the three galvanometers and movement of the three lines towards the centre of the triangle. By adjusting the total amount of light falling on the cells there is one position where the three lines must intersect at one point, which therefore represents directly the location of the colour of the light source under test within the trichromatic system of the triangle.

Thus we have a ready means of measuring the *colour* but not the *colour rendering properties* of a light source. For we also want to know how the appearance of coloured articles and materials, etc., i.e. the colour of the reflected light, will vary with different illuminants.

Secondly the *colour rendering properties* of a light source will depend on its spectral energy distribution, which may be different for light sources of the same colour, that is having the same trichromatic coordinates. [The different colour-

rendering properties of light from a high-pressure mercury lamp and from a tungsten filament lamp in front of which was a filter (daylight blue type glass) were then demonstrated.]

In what manner shall we specify the *colour rendering properties* of a light source? If we consider electric discharge lamps the spectral energy distribution is dependent not only on the nature of the discharge, but on the type and proportions of luminescent materials used to modify the colour of the light. Apart from attempting to modify the spectral distribution in a manner which will give an approximation to daylight, there are many cases where a 'warm' light is required. In these various cases we have to devise methods of appraising the colour-rendering properties of the source.

Already many methods have been suggested, either based on measurements of relative energy or luminosity in various spectral bands, or on the visual judgement of the apparent colour of coloured materials, etc., when viewed under the various light sources. These methods have their uses, but are rather laborious, and liable to give misleading results.

Having, in the photoelectric colorimeter referred to earlier, a very quick method of measuring colour, why should we not make use of this to measure the colour-rendering properties? For example, if we determine the colour of the light source, and also the *colour* of the light reflected from, or transmitted through, a suitably selected group of coloured materials, or filters, the relative position of these points in the colour triangle should enable not only the colour but the colour-rendering properties resulting from the particular form of spectral distribution of the source to be determined. It will be obvious that in this case two sources which appear the same colour but are different in spectral distribution should be differentiated by the different values of the trichromatic coordinates of the reflected or transmitted light, from or through the coloured media.

The attraction of this method is that we use only the internationally agreed trichromatic system, and can make our determinations at routine photometric speeds on one type of apparatus. Also, perhaps equally important, such results are closely related to what we see when looking at coloured articles or materials under different types of illuminant.

Meanwhile we are finding many practical cases where the new line spectra light sources are, on account apparently of their colour, giving better seeing in various industrial operations. For instance, the new mercury light is being used to advantage in collieries on the picking belts to aid the distinction between coal and shale, also in the Rand on ore sorting belts where the presence of gold in ore can be better detected.

In galvanizing, the detection of flaws is made easier and in laundry work, scorches and iron mould show up more readily. In the pottery industry cracks and blow holes are more easily detected in the early stages of firing—and this light has also proved more effective when inspecting for flaws in glass or for dirt in washed milk bottles.

The explanation of the real cause underlying the improved seeing in each of

these cases might be instructive and may possibly be different for each one. I merely mention them to show that the subject is not an academic one.

Sodium lamps on account presumably of their monochromatic character are of course of use where very fine detail has to be detected.

§ 11. INTRINSIC BRIGHTNESS OF LIGHT SOURCES

Under proper conditions of utilization of light for general lighting purposes it does not usually matter how bright the source of light itself is, for the art of diffusing light is well understood although perhaps not always practised. Therefore for general lighting we are more concerned with the brightness of the glassware used in diffusing the light, than with the brightness of the source of light itself.

Source of light	Approximate intrinsic brightness (can./cm ²)
Carbon filament	20
Tungsten filament (gas-filled lamps)	350 to 1,650
Sodium lamps	c. 10
High-pressure mercury 1 atmosphere, 230 v.	160
High-pressure mercury 125 w. pearl bulb	50
Brightness of column alone	
	1,000
Mercury water-cooled, 400 w./cm., 300 v./cm. *	30,000
Mercury water-cooled, 800 w./cm., 400 v./cm. *	60,000
Ordinary carbon arc	13,000 to 17,000
High-current-density carbon arc	50,000 to 80,000

* Starting volts double running volts.

But when used for projection purposes the intrinsic brilliance of the source becomes vital; and it is not always realized how brilliant some of the new sources of light are, over what wide limits their brightness ranges, and what potentialities these have for projection.

Four or five years ago, you will remember, it was found that very great yields of light could be obtained by the passage of electricity through mercury vapour if the pressure of the vapour was increased. Some of the lamps which have resulted from this arc well known now. Others are more experimental.

[Enlarged images of three different types of mercury vapour lamps were thrown on the screen, one a well known lamp widely used for street lighting had a brilliancy of about 160 candles per sq. cm. compared with about 1000 candles per sq. cm. of a tungsten lamp filament. The second lamp was smaller with a high vapour pressure, and had a brightness of about 1000 candles per cm², i.e. some six times

brighter. Another lamp had at the top a water cooled envelope to dissipate the heat from the area round its very small and brilliant discharge column. The brightness was of the order of 30,000 candles per cm^2 or thirty times brighter than the last.]

The increasing brightness obtained with such lamps begins to make them comparable in brilliancy with high current density arcs used for searchlights and cinema projection. We can press our ionized columns further still, the only limit being our ability to carry away the heat. If we do this the quartz lasts only a few minutes or seconds even when cooled with water. [The lecturer then showed a lamp with a brilliancy approaching 150,000 candles per cm^2 a brilliancy comparable with that of the sun.]

The eye is an extraordinarily bad judge of brilliancy. We usually under-estimate enormously a difference which may exist between the brightness of two sources, unless they differ in total candle power, when the brighter source may sometimes be mistaken for the less bright. The table of brightnesses of typical sources will indicate the range which is within prospect. Some of the higher brilliancy sources in this table have not as yet gone beyond the laboratory stage.

This review of some of the techniques in use in the study of lighting and seeing has, I know, been disjointed and incomplete. In the compass of a short lecture this is inevitable. I tried to choose those aspects of the subject which seem to me to give the clearest picture of the art as it is to-day. If anyone troubles to criticize me I know I am vulnerable in my omissions. But I would ask such critics to bear in mind that I set out to demonstrate the state of an art mainly through the techniques which are in use for its study. As these techniques have become available during the past thirty years the art has changed and advanced greatly. Like so many other subjects, however, that of lighting and seeing has been and is held in check by the inevitable tendency of those who practise it to define it at any epoch in terms of the quantities which they can measure and the techniques they can understand. The illuminating engineer of yesterday was the candle power engineer of the day before. He is becoming the brightness engineer of to-day, but as soon as physics has provided suitable and understandable techniques for appraising contrasts he is surely fated to-morrow to become a contrast engineer. Whereas research can stretch out where it pleases, it is difficult for a practical art to advance faster than the established techniques for appraising its merits.

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DEMONSTRATIONS

STRUCTURES PROPOSED FOR PROTEIN MOLECULES

*Demonstration given on 12 November 1937 by D. M. WRINCH, M.A., D.Sc., Oxon.,
D.Sc., Lond., The Mathematical Institute, Oxford*

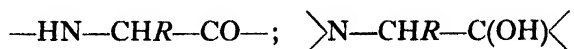
Proteins constitute a large class of chemical substances which take part in a wide variety of biological reactions. The work of Svedberg and his collaborators⁽¹⁾ has shown that there exists a number of proteins which possess a certain molecular status, in that in solutions of appropriate *pH* they consist of globular molecules of definite molecular weight. These molecular weights, it is found, are not distributed at random, but fall into a sequence of widely separated classes. Work on protein films further shows that certain globular proteins in solution spontaneously form monolayers, which have characteristic mechanical properties⁽²⁾.

[Built up protein films by Langmuir and Wrinch and by Wrinch and Marler are shown.]

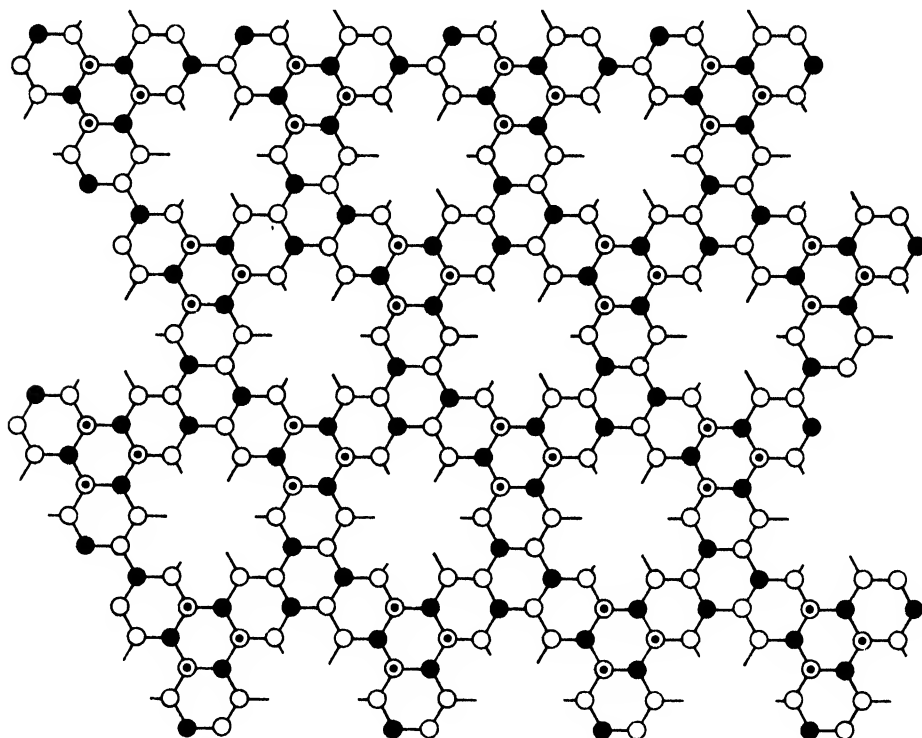
The molecular weights found by Svedberg are very high; they range from 18,000 up to several millions. One specially important class, with molecular weight about 35,000, includes pepsin, insulin and egg albumin. The molecules therefore consist of thousands, some even of tens and hundreds of thousands, of atoms. The comprehensive investigation of possible structures for protein molecules is therefore necessarily a question involving the use of mathematical technique. It is hardly feasible to study the arrangements in space of so many atoms by means of the methods used in classical chemistry.

It is generally agreed that proteins are polycondensation products of amino-acid and imino-acid molecules. Amino-acid molecules $\text{NH}_2\text{—CHR—COOH}$ have in all cases a common skeleton N—C—C . About 25 or 30 different varieties have so far been found among the degradation products of proteins, each characterized by a special *R*. *R* may be purely aliphatic, it may have an aromatic constituent, or it may contain basic or acidic groups. It is a remarkable fact that all these units, whatever *R* may be, prove to have one uniform configuration as regards the C atom carrying the *R* group⁽³⁾. It is further generally agreed that unit is joined to unit in these polycondensation products by the formation of a link between the N atom of one and the terminal C atom of the other. The problem of the structure of proteins therefore requires the consideration of all possible arrangements in space of the building units, unit being linked to unit by $\dots\text{N)—(C}\dots$ bonds. In the cyclol theory of protein structure⁽⁴⁾ an attempt has been made to devise structures fulfilling the given conditions. It is to be regarded simply as a first step towards a comprehensive investigation of the problem which will require the application of group theory and of the theory of partitions and the development of new types of geometry of position.

The amino-acid residue, the building unit for proteins, can be written in two ways:



In the first case only one-dimensional polymers are geometrically possible; these can be open or closed. In the second, two-dimensional or even three-dimensional polymers are geometrically possible. The full geometrical investigation of possible structures for protein molecules which satisfy the given conditions necessarily



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Figure 1. The cyclol pattern. The median plane of the lamina is the plane of the paper. The lamina has its "front" surface above and its "back" surface below the paper. ● = :N; ○ = C(OH), hydroxyl upwards; ⊙ = C(OH), hydroxyl downwards; ○— = CHR, direction of side chain initially outwards; ○- = CHR, direction of side chain initially upwards.

requires the discussion of all these polymeric types. In the polypeptide theory of protein structure only open one-dimensional polymers were contemplated. One-dimensional polymers consisting of as many as 18 units in open chains were subsequently built in the laboratory. These substances proved not to be proteins. Closed one-dimensional polymers, with the exception of diketopiperazine molecules consisting of two units, were not contemplated and have not yet been built in the laboratory. Attention is therefore directed to possible structures consisting of closed one-dimensional polymers and also to two-dimensional or even three-dimensional polymers.

One special class of two-dimensional polymers, the cyclol fabric, has been

investigated in some detail. This two-dimensional atomic network or fabric is shown in figure 1. The uniformity of all the amino acids already referred to implies that such a fabric is dorsiventral; all *R* groups initially emerge from its front surface and none from its back surface. These experimental facts thus find a fundamental interpretation on this theory, suggesting in fact that the essential entity in proteins is a dorsiventral fabric. The findings regarding the existence and nature of protein films thus fall into place in the general scheme. Furthermore, an investigation of the geometrical nature of the cyclol fabric discovers that such a fabric can be folded round so as to lie on the surface on certain polyhedra and form closed, cage-like structures⁽⁵⁾. These it is suggested are the globular proteins which in solution form monolayers simply by the ripping open of these closed cage-like structures. On this view protein monolayers are simply geometrical isomers of globular proteins, and consist of polymers or associations of pieces of the cyclol fabric.



Figure 2. The C_2 structure. [Photograph taken by F. M. Beltjens, Leyden]

The metrical requirements of the constituent atoms show that only certain polyhedra are acceptable, and further that such polyhedral cyclol structures exist in series which consist of specific numbers of units given by quadratic functions of the natural numbers. These deductions explain the results of Svedberg in general terms, each molecular weight class on this interpretation connoting one closed cyclol or an association of a certain number of such cyclols.

At present it has proved possible to construct only one series of closed cyclols $C_1, C_2, \dots, C_n, \dots$. The polyhedral framework in each case is a truncated tetrahedron and the number of units in C_n is $72n^2$. Models of C_1, C_2, C_3 and C_6 are shown. (See also the photograph of C_2 in figure 2.) The C_2 structure containing 288 units is of special interest. Its molecular weight apart from attached water molecules is, say, 36,000, assuming a mean residue weight of 125. The suggestion was therefore made in 1936 that this may be an appropriate structure for insulin, pepsin, egg albumin and the other globular proteins which have molecular weights in the neighbourhood of 35,000⁽⁵⁾. It has since been stated by Bergmann and Niemann⁽⁶⁾ that the chemical analysis of egg albumin allows the deduction that each molecule of this substance contains 288 amino-acid residues. It has further been found that the C_2 structure

fits adequately with the measurements found from the X-ray analysis of the lattices of pepsin⁽⁷⁾ and insulin⁽⁸⁾. It is hoped to subject the predictions of the theory to further and more detailed test by the application of physical techniques, including the use of electron-diffraction.

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MAGNETO-DAMPING IN NICKEL

Demonstration given on 26 November 1937 by MARY D. WALLER, B.Sc., F.Inst.P.

The subject of this demonstration was the outcome of some acoustic studies made on metals and special alloy steels^(1,2) in order to determine how the internal damping is affected by various physical conditions.

A pure hard nickel rod, kindly supplied by Messrs Henry Wiggin and Co., Ltd., was suspended horizontally at the two nodes (0.224 of the length from either end) by means of two fine threads, and struck with a hammer. The note emitted remained audible for some seconds. This procedure was repeated after the specimen had been placed in a magnetizing field of about 100 gauss, when it was found that the note died out three or four times more rapidly. For purposes of demonstration in a large room, a rod about 12 cm. long and about 1 cm. in diameter, which vibrated at 2570 c./sec., was readily audible, but the phenomenon was also demonstrated with a thinner and with a thicker rod.

A typical set of observations, made with the ear in a standard position and using a stop watch is shown in figure 1, in which the abscissa shows the strength of the magnetic field to which the specimen was subjected, while the ordinate shows the subsequent duration of audibility in seconds. The magnetic condition of the rod in figure 1 can be inferred from the hysteresis curve given in figure 2. Points to be noted in connexion with figure 1 are the horizontal part of the curve at *A* for weak fields, the steep part of the curve (corresponding to the steep part of the *AB* hysteresis curve), the impossibility of restoring the vibrating properties except by thoroughly demagnetizing the specimen, and the two maxima at fields which are near to, but exceed the coercivity.

Similar observations have been made with a more highly damped annealed pure nickel rod, and with rods made of commercial nickel, iron, cobalt (kindly given by the Brandhurst Co., Ltd.) and a number of Sir Robert Hadfield's special alloy

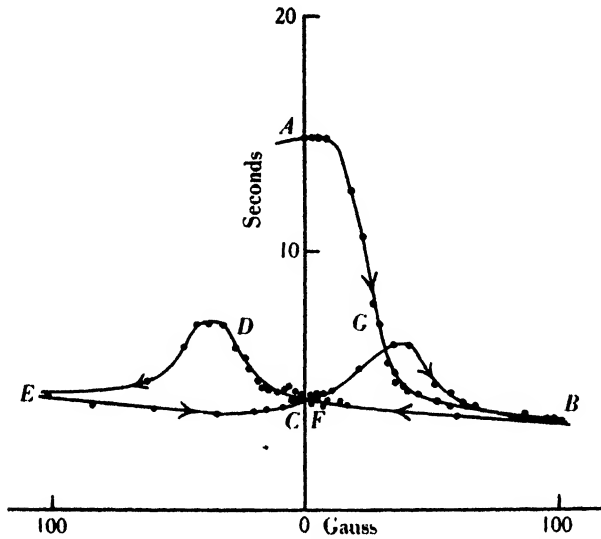


Figure 1. Variation of duration of audibility of vibrating nickel bar with intensity of magnetic field previously used to magnetize it.

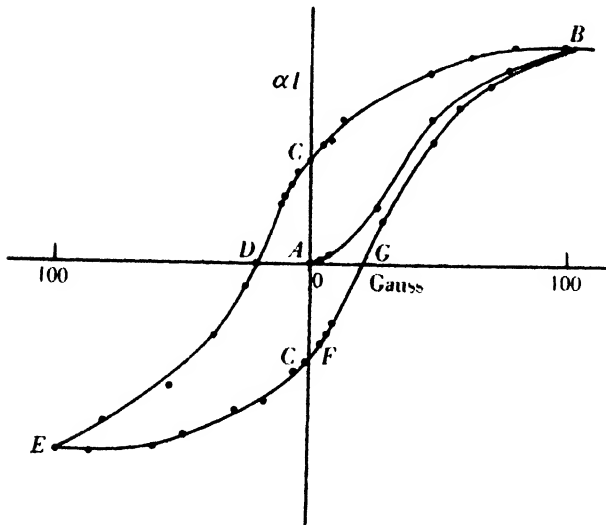


Figure 2. Hysteresis curve.

steels⁽²⁾. The effect is greatest with nickel and greater with cobalt than with iron. Kerston⁽³⁾ has explained the increase of damping which occurs in the magnetized condition as being due to eddy currents occurring in the oscillating body; I have

found that the effect is too small to be detected in some of the magnetic alloys investigated. The increase in damping in the case of nickel is comparable with that which can be produced by suitable mechanical and heat treatment.

Since vibration damping is of considerable importance in engineering practice⁽⁴⁾, and since it is a structure-sensitive property which depends upon so many physical conditions, a simple method of observing it, such as the above, should be of value.

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A PLANE-ELECTRODE DEMOUNTABLE THERMIONIC TUBE USED AS A GENERATOR OF ULTRA-HIGH-FREQUENCY OSCILLATIONS

Demonstration given on 26 November 1937 by W. A. LEYSHON, Ph.D., F.Inst.P.

The apparatus demonstrated was set up with the main object of obtaining more information in regard to the generation of ultra-high-frequency oscillations by a method previously described to the Society⁽¹⁾. In this method an experimental tube was used in which the electrode system consisted of two parallel plane grids at the same positive d.c. potential, with symmetrically placed kathodes external to them. A Lecher-wire system was connected to the two grids.

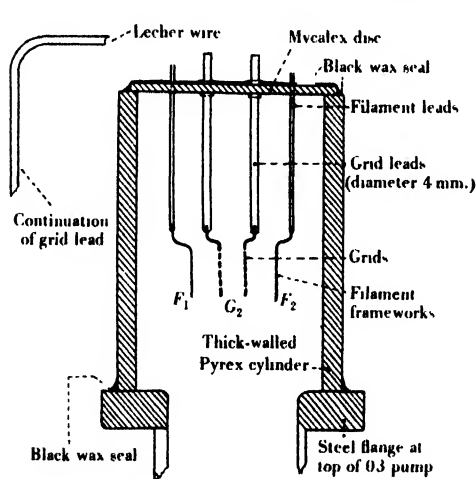


Figure 1.

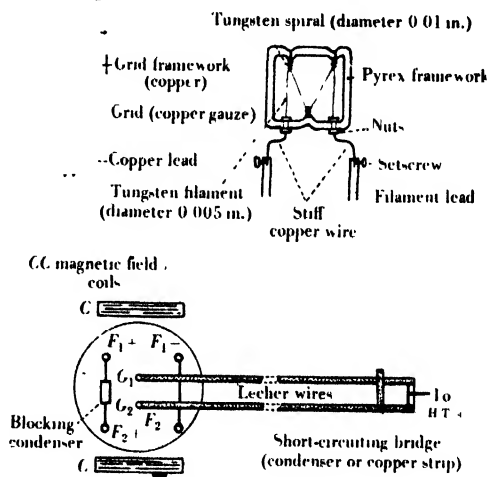


Figure 2.

In the present apparatus simplicity of design and working was aimed at; it may in fact be termed transportable—it has on two separate occasions been transferred to Oxford, without air being let into the tube. The tube is continuously evacuated

by a pumping system consisting of two Metropolitan-Vickers oil condensation pumps (o2 and o3 in series) backed by a Hyvac pump. The construction of the tube is shown in figures 1 and 2. Tungsten wires of diameter 0.005 in. were finally, after a considerable amount of preliminary experimentation, chosen for the filaments. Sufficient emission is obtained with filament currents of the order of 2 amp. Mycalex is used as the material for the lid of the valve because of its low loss at high frequencies. All the demountable joints are sealed with Apiezon black wax.

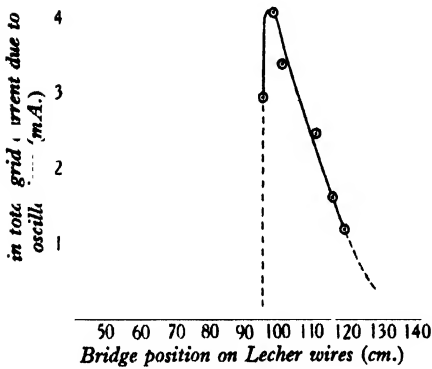


Figure 3. Typical graph showing relation between length of Lecher wires and change in grid current. Valve 8: $v_{g1}=v_{g2}=186$ v.; $i_{g1}+i_{g2}=25.5$ mA.

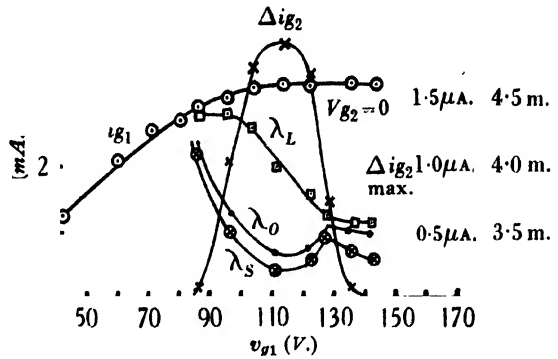


Figure 4. Valve 5: One (F_1) filament emitting; outer grid G_2 at zero potential; i_{g1} , current to inner grid G_1 ; Δi_{g2} , change in current to outer grid G_2 due to oscillation; λ_L , λ_O , λ_S , longest, optimum and shortest wave-length generated.

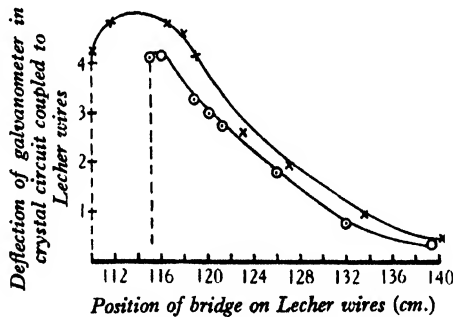


Figure 5. Showing effect which may be produced by the application of a longitudinal magnetic field. Valve 10: $v_{g1}=v_{g2}=70$ v., $i_{g1}+i_{g2}=4.85$ mA.; \odot without magnetic field; \times with magnetic field (ca. 12 gauss).

The Lecher wires are copper tubes of the same diameter as those used as electrode leads inside the valve, and they are at the same distance apart as these leads. Thus, as will be seen from figures 1 and 2, the Lecher-wire system is practically continuous up to the electrodes (grids) themselves.

Degassing, which in the first instance took some considerable time, is assisted by internal heating due to the hot filaments and, when the vacuum is sufficiently high, by bombardment with electrons and positive ions. At a later stage of evacuation this process is further accelerated by the generation of high-frequency oscillations.

tions. The degree of vacuum is estimated by the backlash ratio, i.e. the ratio of (positive) outer grid current to (negative) inner grid current, the inner grid (i.e. that nearer the emitting filament) being held at a potential of 160 v. and the outer at -4 v. relative to the negative end of the filament. It is found that oscillations will, in general, start when this ratio is of the order 5×10^{-5} . The limiting ratio attainable with no special arrangement for cooling the wax seals, or for shielding them from bombardment by stray electrons, is about 2.5×10^{-5} . For the electrical circuit use is made of the 220 v. d.c. mains to provide both filament current and high tension, or part of the latter. It will be noted, figure 2, that the negative ends of the filament leads are connected directly, and the positive ends through a blocking condenser. The possibility of large ultra-high-frequency variations of cathode potential due to standing waves on the filament connecting wires is thus minimized.

With this apparatus a large number of observations have been made in order to find out how the generated wave-length depends on the length of the Lecher wires, the distance between the electrodes, transparency of the grid, the applied voltages, the cathode emission, and the applied magnetic field. The investigation is not yet complete, nor is the apparatus in its final form. However, a great many of the observations previously recorded for plane or cylindrical valves have already been repeated with it. Some typical results are shown in figures 3 to 5.

The tube can be made to act as its own degassing agent, by heating, bombardment, and generation of ultra-high-frequency oscillations; it can be made to give an indication of the degree of vacuum reached within it; the attached Lecher-wire system can be used for the measurement of the wave-length of the oscillations generated, and to give information in regard to the effective impedance of the electrode system at the frequency of these oscillations. In a perfected form (in which it is possible to adjust the distances between the cathodes without the tube having to be demounted) the apparatus should be useful for teaching purposes.

The cathode frameworks and other parts of the valve structure were made in the Electrical Laboratory at Oxford, where Prof. Townsend has most kindly allowed me to work during summer vacations. The cost of the research has been covered by grants from the Waller Research Fund.

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REVIEWS OF BOOKS

An Outline of Atomic Physics, by Members of the Physics Staff of the University of Pittsburgh. Pp. ix + 414. (John Wiley and Sons Inc. New York. Chapman and Hall Ltd. London. Second Edition. 1937.) 18s. 6d. net.

The book grew out of a course of lectures designed for college students who, having completed a year's work in physics, were proceeding to qualify themselves for some other profession. It was hoped, by taking them to the frontiers of physics and giving them some intelligent appreciation of what was going on there, to awaken in them a love of it and a respect for its achievements; feelings which a first-year course in physics too often leaves unstimulated. The book covers the range of subjects to be expected from its title, and in addition there are chapters on the kinetic theory of matter and on astrophysics.

The book admirably fulfils the purpose for which it was designed. While avoiding the mass of detail and the formal mathematical development which are essential in a textbook for specialist students of physics, the authors are not afraid of making calls on the intelligence of the reader, and for the most part succeed in conveying the physical argument in a clear and intelligible form. The book is illustrated with photographs and numerous diagrams. For the second edition it has been thoroughly revised in the light of recent discoveries, and a new chapter on nuclear structure has been added.

J. A. C.

Hydro- and Aerodynamics, by S. L. GREEN. Pp. viii + 126. (London: Sir Isaac Pitman and Sons, Ltd.) 12s. 6d.

Where *does* the student of physics, or of mathematics, acquire his introduction to the theory of the motion of fluids? Clearly, if he is to carry the matter far, he will have to read Lamb at some stage (and do let us disabuse our students of the idea that it is difficult, or that it involves very advanced mathematics), but with what shall he precede this? The textbooks of theoretical physics generally contain a chapter or two on the subject, but since Besant and Ramsey fell into disuse there has been no good introduction, as far as the present reviewer is aware.

Without question, this book fills the gap for the student of mathematics. It contains the necessary minimum to enable it to serve as a starting point, whatever road the student is intending to travel later: the equations of motion of the inviscid fluid, irrotational motion and the application of conformal transformations both to continuous and to jet-like flow, vortex motion and wave motion, with a final pair of chapters on viscous fluids and on flow at high Reynolds numbers. In these last two chapters the treatment is fragmentary and would for most readers require supplementing by a more physical treatment such, for example, as is found in treatises on general physics. Although the subtitle states that the book is for advanced students of aeronautics, hydraulics, physics and mathematics, there is little discussion of gases (the flow of a viscous fluid through a tube is only carried out for the incompressible case) and no discussion of the resistance of bodies at moderate and high Reynolds numbers. It is not suggested that this last could be treated in any detail, since mathematical advances are only now proceeding in a halting manner; but an indication of the nature of the results, and an explanation of the utility of dimensional theory, would have added to the value of a book which is already extremely good.

J. H. A.

Sound, by A. T. JONES. Pp. xii + 450. (Chapman and Hall). 20s.

Dr Kaye in his Presidential Address before Section A of the British Association said that "acoustics, far from being a Cinderella, has become a radiant Princess of physics in whose career the public interest has become completely enchained". One illustration of this fact is the increasing number of textbooks on academic and applied acoustics which are now appearing, a symptom of the interest which universities are taking in this subject. The textbook which Prof. A. T. Jones has written is remarkable for the amount of advanced acoustics it covers without the use of complicated mathematics. In fact, it almost entirely avoids mathematics. (An indication of the type of reader for which it caters can be obtained from the footnote on p. 28: "If the reader has forgotten what a logarithm is, he may refer to Appendix 4"). This does not mean that the mathematics is replaced by tedious argument—far from it. The explanations are almost invariably brief and interesting. A remarkable feature of the book is the sets of problems which appear at the ends of the sections. These are not set to test book knowledge, but always to extend the reader's learning by making him think beyond what has been discussed. Sometimes they do more than this, even; for example: "What is the objection to explaining thunder by the bumping of clouds together?" Another question is rather longer; "A story was once written about an Arctic expedition on which the men encountered a bitterly severe cold spell. The cold was so intense that the men had difficulty in understanding each other and finally were unable to hear at all. Their words were frozen before there was time for them to be heard. When the cold became less intense the frozen speech began to thaw out and words and sentences spoken days or weeks earlier were heard at last. We smile at this story, but what is the matter with it?" It is just possible that questions of this type will render a lecturer's life a little more arduous. Another form of this question appears in connexion with electrically maintained tuning forks. After devoting a paragraph to putting forward an explanation of the action of a maintained tuning fork, he puts the question: "What is the fallacy in the above argument?"

The book contains the usual chapters on vibrating motion, combination of tones, musical scales, sound transmission, free and forced vibrations, speech and hearing, musical instruments and technical applications. Of these one might single out the chapters on speech and hearing, musical instruments, and technical applications as being especially good. There are one or two misprints and one or two comparatively unimportant errors. Doubtless these will be put right in the next edition.

The book may be recommended to physics students, musicians and the general public alike.

J. E. R. C.

A Text-book of Light, by G. R. NOAKES, M.A. Pp. x + 355. (London: Macmillan, 1937.) 6s.

This book is intended for students working to the syllabuses for the higher school certificate, university scholarships, first M.B., etc. It incorporates many of the recommendations in the Physical Society's *Report on the Teaching of Geometrical Optics* (1934), including one of the two alternative sign conventions in which focal length and dioptric power take the same sign, instead of opposite signs as in the Cartesian system used in the older textbooks. The convention chosen by the author is the non-Cartesian one in which all real distances are positive and all virtual distances negative; the reasons for the choice are that pupils consider it to be less artificial than the older Cartesian system and that the average worker makes fewer slips. It is for these very reasons, however, that many teachers prefer the other alternative recommended in the *Report*, namely the Cartesian system in which the initial direction of the light is taken as positive. The calculus is used, and photometry, optical instruments, polarization, ultra-violet radiation and X rays are dealt

with at some length. In the reviewer's opinion, photometry is dealt with much too early, as in many elementary books on geometrical optics. The text is illustrated with 276 figures, which, with few exceptions, are carefully drawn. Notable exceptions are figures 20 (Lummer-Brodhun photometer), 104 (Pulfrich refractometer), 107 (erecting right-angled isosceles prism) and 208 (prism spectrometer), all of which might well be improved in a future edition. Examination questions are given at the ends of chapters, and the answers at the end of the book.

W. J.

Fundamentals of Physical Optics, by FRANCIS A. JENKINS and HARVEY E. WHITE.
Pp. xiv + 453. (New York and London: McGraw Hill, 1937.) 30s. net.

Starting where the simple principles of geometrical optics leave off, the authors have devoted the whole of this book to the so-called classical physical optics or wave optics, to the exclusion of any systematic discussion of the quantum theory and its application to spectra and atomic structure. The reason for this is twofold: consideration of space, and the recognition of the complementary wave and quantum aspects of light as equally important, but quite distinct, fields of knowledge. In covering only the first field, the book has achieved a unity which would have been lost by the inclusion of a necessarily brief treatment of the second. Nevertheless, in the later chapters dealing with the interactions of light and matter, the authors have been careful to point out the limitations of the classical wave theory and the necessity of the quantum theory for a complete explanation of observed phenomena. The choice of subject-matter and method of development are the result of many years of teaching by Prof. R. T. Birge, the authors, and others in the department of physics in the University of California, Berkeley. In the development of the subjects of interference, diffraction, dispersion polarization, etc., emphasis is placed on the physical explanation of the phenomena, and graphical or vector methods are freely used to supplement the mathematical treatment. In addition there are chapters on fluorescence and phosphorescence, light-sources, dielectric and metallic reflexion, electromagnetic theory and magneto-optics and electro-optics. The text is illustrated throughout with diagrams and photographs, most of which are by the authors themselves. It is in classical physical optics that perhaps the most beautiful and striking experimental demonstrations in physics are to be made. Descriptions of many of these are given throughout the book, divided from the main text by horizontal lines. Another pleasing feature is the inclusion of brief biographical footnotes. Each chapter ends with a number of problems. The book is well indexed, excellently produced, and can be unreservedly recommended to honour students.

W. J.

Trigonometry: Part II, Higher Trigonometry, by T. M. MACROBERT and W. ARTHUR.
Pp. xiii + 137. (London: Methuen and Co.)

Starting as the study of triangles, an adjunct of geometry (the measurement of land), trigonometry soon finds the advantages of introducing the sine, cosine and tangent. We may, for the purposes of classification, say that elementary trigonometry considers these in their geometrical aspects, but when they are studied for their own intrinsic interest we soon find that they are intimately related to the exponential function, and therefore of course to its inverse, the logarithmic function. Consequently they are appropriately studied in courses of analysis, or in the theory of functions, and the methods of these sciences are helpful. In previous generations it was the custom, either in the spirit of mortifying the flesh or else from a Houdini-like joy in overcoming obstacles, to write books on higher trigonometry in which the results obtained elsewhere by the methods of the

calculus were deduced by pure algebra. This rather pointless procedure has now been dropped, and in the book under review the most convenient method available is used in each case. It is not intended for advanced students, and therefore opens with chapters on complex numbers and, after proving de Moivre's theorem, proceeds to the familiar applications in various fields. It then takes up the notion of a limit, deals with those various finite and infinite trigonometrical series which most of us can never remember without a book of reference, and concludes with a good treatment of the logarithmic function. On the way various useful sidepaths are explored, such as the evaluation of certain types of definite integral. The book is certainly one to recommend, and not least among its virtues are the very numerous, well-chosen exercises.

J. H. A.

Science and Music, by Sir JAMES JEANS. (Cambridge University Press.)

This book is a welcome addition to those which seek to explain to the musician the working of his tools, and it is sincerely to be hoped that he will take advantage of it. Musicians are notoriously supercilious about acoustics, pointing out that their art was old when the science of acoustics was still young, and that—as the physicist would be the first to admit—the science has still some leeway to make up before it is abreast of the empirical discoveries of the musical instrument makers. The reputation of Sir James Jeans as scientist and author is such that musicians can scarcely ignore the experimental science of recent years, where it touches music. In particular, we hope that the author's exposure of the psychological self-delusion involved in the appraisal of "pianoforte touch", "key character", etc., will sink in. No one could write a book of this nature without drawing on the resources of his predecessors, and Sir James Jeans is quite frank in this matter. It was his intention, he tells us, to bring Helmholtz up to date, but the book as it stands is better than that; it deals with all the aspects of playing and listening to music on which physics has anything to say. Indeed, the section which is mostly Helmholtz, that on musical scale, is perhaps the least inspiring part of the book, though it must be very difficult to make these matters plain to a person who lacks a mind for figures. In only two respects does one feel a deficiency in the book. We should have liked something about the voice as a musical instrument to supplement a good chapter on hearing, and some account of the working of instruments in which the sounds are electrically produced. But perhaps the author, as an organist, joins the ranks of those who deplore such imitations, though it is time for the Hammond electric organ to get a paragraph. In short, a book which should appeal to all whose interests are both musical and scientific

E. G. R.

Personality Survives Death, by LADY BARRETT. With a foreword by Canon R. J. CAMPBELL. Pp. xlv + 204. (Longmans Green and Co.) Price 7s. 6d. net.

Coming as it does from the pen of one so established in the scientific world, this book cannot fail to arouse interest in those quarters. The writer styles herself editor of the messages contained therein, which purport to be communications from her late husband, Sir William Barrett, F.R.S. As founder, in 1881, of the Society for Psychical Research, he was wont to state that his interest in psychical research arose out of his experience as a physicist. There seems to be nothing in this small volume in disaccord with that statement. It is apparent that the matter contained in the messages owes its origin to a scientifically trained intellect which is not likely to be that of the medium. The initial difficulty experienced by most enquirers—namely, the reason for so many apparently futile communications—is dealt with more satisfactorily than in previous publications on the subject. And there is scarcely a sentimental word. Certain of the tests recorded leave the reader with but two alternatives—either to accept the message as genuine or to doubt the veracity of the recorder.

An interesting study for those of sceptical mind.

L. P. T.

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THE RATE OF VISCOUS FLOW OF METALS: PART 1, TIN

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ABSTRACT. A description is given of a new method of determining the dependence of the rate of viscous flow of metals on the deforming force and its variation with temperature. The measurements were made by means of an optical lever system, and the effect of changes in length produced by possible temperature fluctuations in the furnace were eliminated by the use of a second wire as a support for the lever.

It has been found that, for tin, for very small extensions the velocity of viscous flow v can be considered independent of time, but is connected with the stretching load P by an exponential relation for any given temperature and with the absolute temperature T by an exponential relation for any given load. Different relationships of the form

$$v = \delta e^{\beta PT - \alpha P + \gamma T},$$

where α , β , γ and δ are constants, have been obtained, from the {flow, load} curves, for the rates of flow of tin for glide in one and two directions respectively, and the relations are probably of the type

$$v = K \{e^{\beta (P+P_0) (T-T_0)} - 1\},$$

where K , β , P_0 and T_0 are constants. Evidence has been obtained in support of the view that the temperature of the allotropic modification from β to γ tin takes place at 203°C . and not at 161°C . The loads for transition from single to double glide and the breaking loads have been shown to be connected with the corresponding temperatures by a hyperbolic expression. Finally, the behaviour of the tin wire has been shown to be in general agreement with the results obtained from single crystals.

§ 1. INTRODUCTION

WHEN a metal is strained beyond the elastic limit, deformations take place which are a function of time. Of late years this phenomenon has been the subject of extensive researches embracing both engineering-scale creep experiments and the study of glide in single crystals. This work has been fully discussed in recent books^(1, 2, 3, 4).

The present research was undertaken, at the suggestion of Prof. Lees, to investigate the viscous part of the flow in metal wires, over a large range of loads, from

air-temperatures to the melting-points of the materials. The experiments were commenced on tin, which shows all the plastic phenomena at ordinary temperatures and has the lowest melting-point of the metals easily obtainable in the form of wire.

§ 2. EXPERIMENTAL METHOD

As the metal wires were to be maintained at a uniform temperature over a wide temperature range the apparatus had to be compact, and wires 5 cm. in length were used. They were suspended in a vertical furnace, whose temperature was measured by thermocouples. Two wires were employed, one under constant load acted as standard, thereby eliminating errors due to thermal expansion and small fluctuations of temperature, while the other was subjected to various loads, the extension causing a tilting of an arm, supported by the wires, which was in turn measured by an optical lever system.

For the small loads used, the percentage elongation and diminution of cross section of the wires were too small to make it necessary to take the latter into account. With larger loads the decrease of cross section was not uniform, but local thinning occurred. The present experiments were therefore performed under constant load, provided by a scale pan and ordinary weights.

§ 3. DETAILS OF THE APPARATUS

The complete apparatus is shown in figure 1, details of it being as follows.

The furnace. This consisted of an alundum tube *A*, on which the heating coil was wound. It was surrounded by lagging *B*, and enclosed in a sheet iron jacket *C*, the ends being closed with slabs of sindanyo *D*, which were bolted together by steel stays *E*, the ends of which served as terminals for the furnace winding. The whole was supported on stout iron legs *F*. The top of the furnace, above the apparatus, was filled with a plug of asbestos wool and covered with a sindanyo cap. An iron tube (see below) fitted into the interior of the furnace and with the outer iron jacket *C*, acted as isothermal surfaces which helped to maintain uniformity of temperature along the axis of the furnace. The heating current was taken from the 240 volt mains, and measured by an ammeter, small fluctuations being adjusted by means of the resistances in series with the furnace.

Methods of supporting the wires. The ends of the wires were gripped in a pair of steel jaws *G*, which could be screwed together, one of them being bolted to a square bar of sindanyo *H*. This refractory material which is easy to work, has a fairly high tensile strength and a low thermal conductivity, which helped to diminish losses from the ends of the wires. These bars, supporting the wires, were themselves fastened, side by side, by passing them through holes in a disc of steel *J*, being kept in position by small steel pins *K* passed through the bars. This steel plate rested on three pegs projecting from the inner walls of an iron tube *L*, which fitted closely into the furnace. The bottom of the tube was bolted to a disc of sindanyo *M*, having a rectangular hole cut in its centre, through which the bars attached to the lower ends of the wires passed. The disc also acted as a screen to prevent direct radiation from the furnace to the mirror system. It was supported by three brass legs *N* with

adjustable feet, so that the apparatus could be levelled to let the wires hang vertically. Thus the wires were supported in the middle portion of the furnace, symmetrically about its axis, and maintained at the same uniform temperature along their length. The lower ends of the wires were gripped in the same way and supported sindanyo bars *O*, which projected below the disc. Strips of steel were bolted to the bottom ends of the bars, and in turn carried steel tables *P* to support the mirror system. A hook was attached to the experimental wire and passes through a hole in the bench to support the scale pan and an applied load.

The mirror system. A mirror *Q* was attached at an angle of 60° to the bottom of a U-shaped piece *R*, balancing weights being placed on the other ends. On the under side of the U piece there were two pairs of hardened steel knife-edges, which rested on the tables *P*. The table on the experimental wire had a notch cut in its surface into which one pair of the knife-edges fitted, while the table on the standard wire was left smooth. The presence of the knife-edges on the mirror arm ensured the constancy of the distance between them and eliminated any effect which might have been caused by the wires moving nearer together or farther apart, while the notch on the table of the experimental wire kept the mirror in the same position and no transverse motion of the mirror was caused by the tilt.

The mirror reflected light from an illuminated scale into a telescope, where the scale deflection was observed.

Let e be the extension of the wire of length L , and b the distance between the knife-edges of the mirror arm, which is thus tilted through an angle ϕ given by

$$e/b = \tan \phi = \phi,$$

assuming the angle to be small. The beam of light from the scale reflected into the telescope moves through an angle 2ϕ , which, if δ is the scale deflection and λ the distance of the mirror from the scale, is given by

$$\begin{aligned}\delta/\lambda &= \tan 2\phi = 2\phi \\ &= 2e/b\end{aligned}$$

and

$$e = \delta b/2\lambda.$$

Now $b = 0.990$ cm. and $\lambda = 273.9$ cm., therefore a scale deflection δ of 1 cm. means an extension of the specimen of $e = 0.001807$ cm. The specimen is of length 5 cm. and as the scale reading can be determined to 0.01 cm., the apparatus is capable of recording changes as small as 0.0000036 cm. per cm. length, or approximately four parts in a million.

§ 4. MEASUREMENT OF TEMPERATURE

Thermocouples and method of mounting. Two stout thermocouples *T*, of 22 s.w.g. Hoskin's alloy wire (chromel and alumel), with junctions on the axis were used to measure the temperature of the furnace in the near neighbourhood of the wire. The junctions were formed by silver solder. The leads were mounted in silica twin-bore tubes *S*, which were encased in thin brass tubing to give them greater strength. They passed down the inside of the steel tube and out through the sindanyo slab to the cold junction, being insulated by glass tubing.

The cold junction. This consisted of a short length of brass tube, about 4 cm. in diameter, which had its bottom plugged up with a wooden block. The tube was filled with mercury and closed with a cork, through which passed four small glass tubes, immersed in the mercury, whose temperature was given by an accurate mercury-in-glass thermometer. The small glass tubes were filled with mercury, and the leads of the thermocouples rested in them, along with the copper leads from the potentiometer, used to measure the e.m.f. generated. The brass tube was covered with baize to prevent heating by radiation from the furnace.

Calibration of thermocouples. The e.m.f. of the thermocouples was balanced in the usual way against a standard cell, an ionization potentiometer by Tinsley being used. The two thermocouples were found to give almost identical readings at the various fixed points employed in the calibration, as shown in the following table 1.

Table 1. Cold-junction temperature, 20.0° C.

Fixed point	Temperature (° C.)	E.m.f. (mv.)	
		Thermocouple 1	Thermocouple 2
M.p. ice	0.0	-0.78	-0.78
B.p. water	100.0	3.21	3.21
B.p. aniline	184.1	6.56	6.56
M.p. tin	231.9	8.50	8.49
M.p. cadmium	320.9	12.26	12.26
M.p. sulphur	444.3	17.53	17.53

§ 5. CONDUCT OF EXPERIMENT

Before an experiment, the specimen of wire was suspended in the furnace, with a load of 200 g. on its lower end to keep it taut, and heated to 200° C. It was allowed to remain at this temperature for a few minutes and then slowly cooled in the furnace. Portions of the wire were fastened in the steel jaws, which were placed exactly at either end of a steel standard of length, thus ensuring that the wires were always the same known length (4.99 cm.). The apparatus was then set up and the furnace heated up to approximately the desired temperature, when the current was reduced to a value which would maintain the furnace temperature constant at the required value. It was found that variations of temperature along the specimen, or due to current fluctuations, were never more than 1 or 2 per cent.

After the temperature had remained steady for some time the experiment was commenced. The scale pan was placed on the hook, and the immediate deflection was observed in the telescope. Scale readings were then taken at 2 min. intervals, until the rate of increase of length with time became constant. The load was then increased, and the experiment repeated, and so on until the rate of extension became so great that it was impossible to take further observations, or, in some cases, till the wire broke. It was found that the rate of flow soon fell to a constant value, and usually readings over a period of 15-20 min. were taken for each load. By taking comparatively short time periods, the value of the flow was obtained without any appreciable reduction in cross-sectional area, which occurs over long periods.

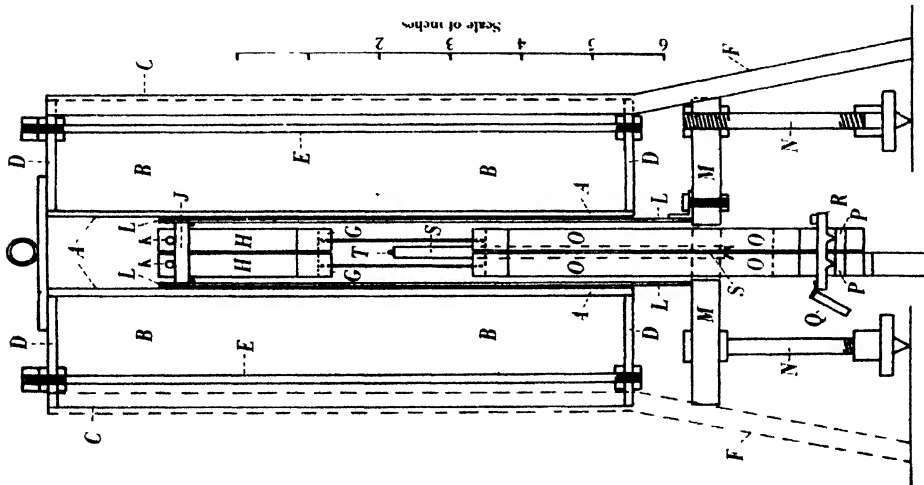


Figure 1. Diagram of apparatus.

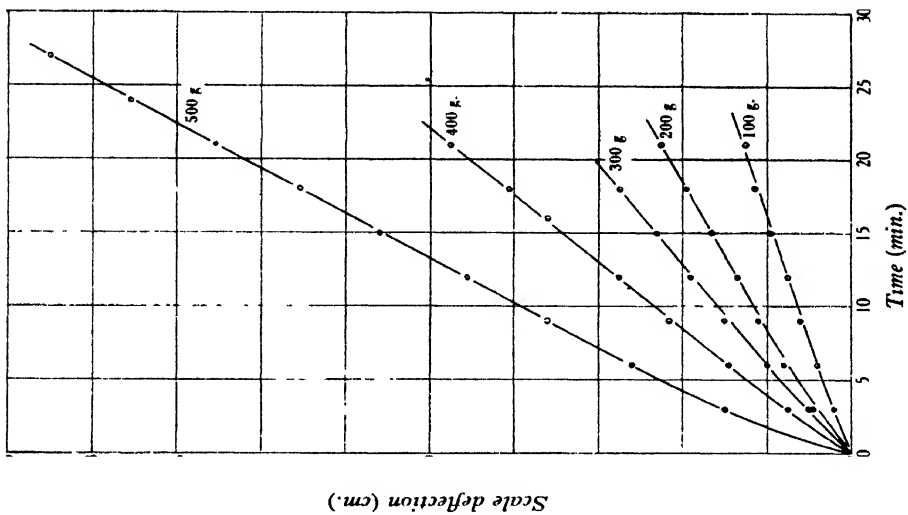


Figure 2. {Extension, time} curves at 101.8°C . for loads of 100 to 500 g.

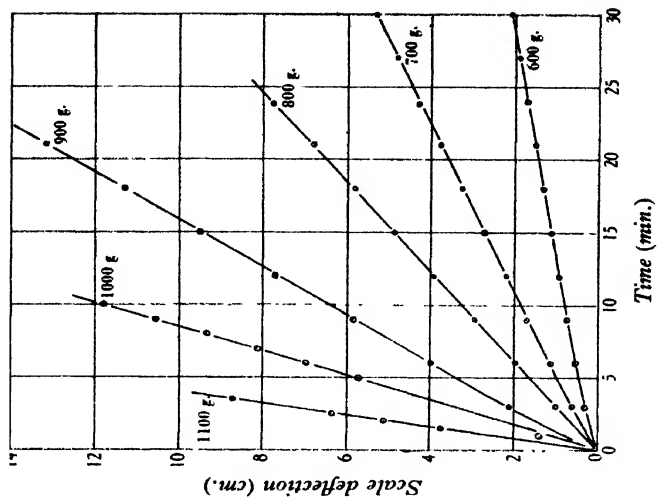


Figure 3. {Extension, time} curves at 101.8°C . for loads of 600 to 1100 g.

It was not considered necessary to anneal the wire, before the experiment with the new load, since Shoji⁽⁵⁾ obtained the same values for the final flow of his wires in the two cases, when between increases of load he had (i) unloaded the wire and annealed it at the same temperature as before the commencement of the experiment, and (ii) only unloaded the wire for a period of 10 hours.

§ 6. EXPERIMENTAL RESULTS

Experiments have been performed from air-temperatures up to 200° C. at intervals of approximately 25° C., the increments of load used being 100 g., except in the case of the experiments carried out at 200° C. when 50 g. stages were used to increase the number of possible observations. The material used was white tin wire of no. 16 s.w.g. and density 7.291 g./cm³.

At lower temperatures it was found that a load could be applied to the wires without causing visible viscous flow, but as soon as a certain value of the load was exceeded a small but definite flow was obtained, the rate of flow increasing rapidly

Table 2. Experiment performed at 102° C. The furnace was heated by a current of 1.5 amp., which was reduced to 1.0 amp.

Load (g.)	Scale reading (cm.)	Initial deflection (cm.)	Subsequent deflection (cm.)	Time	Time interval (min.)	Cold-junction temperature (° C.)	E.m.f. (mv.)
300	15.79	0.14		11 h. 27 m.		22.0	
	15.65			27	0		
	15.56		0.09	30	3		3.20 (1)
	15.49		0.16	33	6		3.18 (2)
	15.43		0.22	36	9		
	15.38		0.27	39	12		
	15.32	0.16	0.33	42	15	22.2	3.20 (1)
	15.26		0.39	45	18		3.18 (2)
	15.20		0.45	48	21		
	15.04			48	0		3.19 (1)
	14.94		0.10	51	3		
	14.84		0.20	54	6		3.18 (2)
	14.74		0.30	57	9		
	14.66		0.38	12 0	12		3.19 (1)
	14.58		0.46	3	15		
	14.49		0.55	6	18		3.17 (2)
900	16.00			2 24		22.9	
	15.52			24	0		
	13.90		2.10	27	3		3.22 (1)
	12.04		3.96	30	6		3.20 (2)
	10.16		5.84	33	9		
	8.30		7.70	36	12		
	6.50		9.50	39	15		3.20 (2)
	4.70		11.30	42	18		3.22 (1)
	2.82		13.18	45	21		
						23.0	

Mean temperature of the cold junction

22.5° C.

Mean e.m.f. of thermocouple 1

3.20 mv.

Mean e.m.f. of thermocouple 2

3.18 mv.

Mean e.m.f. of thermocouples

3.19 mv.

Mean e.m.f. of thermocouples, corrected for cold junction at 20.0° C.

3.28 mv.

Mean temperature of specimen (from calibration curve)

102° C.

with further increase of load. It was also noticed that with increase of temperature this necessary initial load decreased in value until at 223° C. the wire collapsed merely under the weight of the sindanyo bar attached to it, i.e. a load of 51 g.

The three definite types of extension were obtained, namely: (a) the immediate extension on loading; (b) the initial flow, which gradually died out; and (c) the elongation which continued at a constant rate. Since the apparatus was designed to measure small changes in length, for heavy loads the initial extension was too large to be measured, and special arrangements would have to be made if accurate measurements of this quantity were required. Naturally, some measure of the

Table 3

Experimental temperature (° C.)		19	50	79	102	129	158	182	207
Load on wire (g.)	Stress (kg./cm. ²)	Rate of extension (10 ⁻⁸ cm./sec. per cm.)							
150	7.4								22.9
200	9.9								62.0
250	12.3			6.02	8.13	15.1	19.3	44.0	141
300	14.8								556
350	17.3			7.53	12.0	24.1	36.1	82.0	1658
450	22.2	1.08	3.67	10.1	18.1	40.4	63.8	158	
550	27.2	1.39	4.94	15.1	26.8	66.8	114	419	
650	32.1	1.99	6.87	19.3	39.8	105	223	1687	
750	37.0	2.71	9.89	28.1	63.2	193	548	5902	
850	42.0	3.74	12.7	39.1	104	386	1440		
950	46.9	4.93	16.5	55.4	193	819			
1050	51.8	6.45	21.0	86.1	370				
1150	56.8	8.43	26.6	155	723				
1250	61.7	11.2	34.0	281	1481				
1350	66.6	15.0	51.8	524					
1450	71.6	19.9	77.1	904					
1550	76.5	25.9	117	1566					
1650	81.5	35.7	176	3011					
1750	86.4	51.2	269	4909					
1850	91.3	76.8	440						
1950	96.2	112	939						
2050	101.2	162	1192						
2150	106.1	229							
2250	111.1	324							
2350	116.0	495							
2450	121.0	668							
2550	125.9	940							
2650	130.8	1379							

initial flow can be obtained from the {extension, time} curve for each load, but since this effect depends very largely on the previous history and treatment of the specimen, and further, like the immediate extension, is an additive effect, the method of experiment was not suitable for giving values on which great reliance could be placed. However, the rate of constant flow is a factor which is quite independent of previous loads to which the material may have been subjected, and for given temperature conditions is solely dependent on the stress. Moreover, the method adopted has the advantage in that, as the load is applied in stages, the initial flow phenomena also take place in stages, and thus for any given load their effect becomes negligible much more rapidly than it would for the same load applied to an unstrained wire. Table 2 gives an abstract from a typical set of experiments performed at 102° C.

The general type of {extension, time} curves obtained is shown in figures 2 and 3 for the experiment at 102°C. , with time as abscissa and the extension, in scale divisions, as ordinate. The curves illustrate the way in which the higher rate of flow

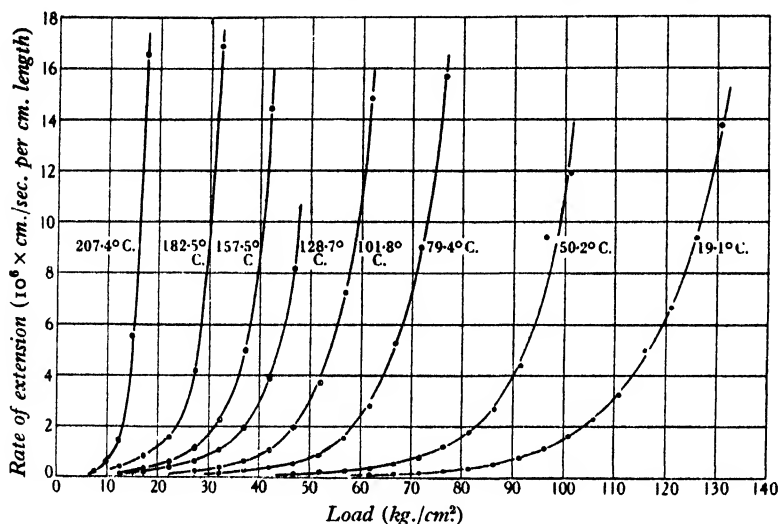


Figure 4. Curves showing relationship between the rate of extension and load for different temperatures.

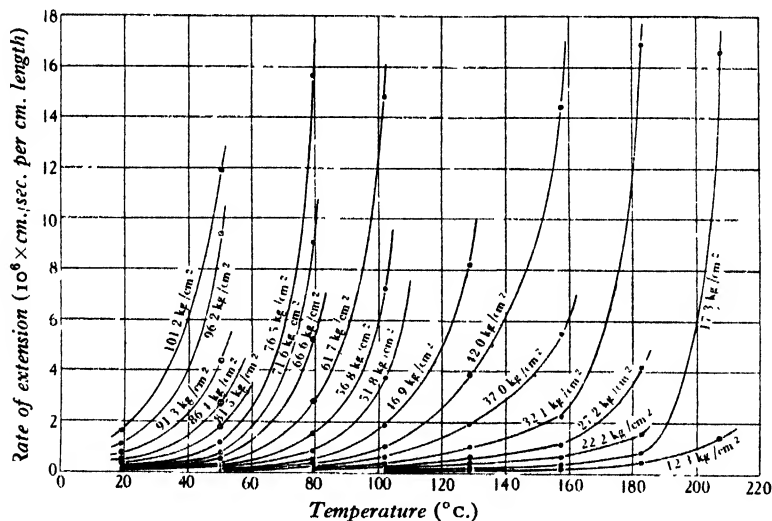


Figure 5. Curves showing the relationship between the rate of extension and temperature for different loads.

soon falls to the steady constant value given by the linear portion of the curve. They also serve to indicate the increase in the final rate of flow with increase of stressing force, but this point is more clearly demonstrated in figure 4.

The diameter of each specimen was measured, but it was found that the deviation of each specimen from the mean value was so small that the mean value was

used for calculating the original cross-sectional area and the stress per unit area for any given load.

The values of the load (g.) applied, the stress (kg./cm²) and the rate of viscous flow (cm./sec. per cm. length) given by the linear portions of the {extension, time} curves are given for each of the temperatures, and are shown in figures 4 and 5. In figure 4 the loads are abscissae, and the rates of flow are ordinates, the curves being drawn for each temperature investigated. These curves are in agreement with those of previous workers and show the initial gradual increase of the rate of flow with load, the subsequent more rapid increasing rate of flow and the final rapid rate ultimately producing rupture.

In figure 5 temperatures are abscissae and the rates of flow are ordinates, the curves being drawn for constant load. They are similar to the {rate-of-flow, load} curves, but show noticeable irregularities at the higher temperatures.

It can be seen from the {rate-of-flow, load} curves at small loads that the least load P_E necessary to cause flow cannot be determined graphically.

§ 7. THE RELATION BETWEEN THE VELOCITY OF FLOW AND LOAD

The {velocity-of-flow, load} curves at constant temperature appear to be of the form

$$\text{velocity of flow} \propto e^{n(\text{load})},$$

where n is a constant, and plotting \log_e (velocity of flow) against load gave straight lines as shown in figure 6, where $\log_e v$ are ordinates and loads P abscissae, hence

$$\log_e v = \log_e A + BP.$$

For a definite value of the load, depending on the temperature, the slope of the curves (with the exception of the experiment performed at 207° C.) undergo a sudden change, thus the curve really consists of two intersecting straight lines.

The values of the slopes B and the intercepts $\log_e A$, from which the constants A are calculated, are given in table 4, for both the slopes of the straight lines, together with the transition loads for each temperature examined.

Table 4

Temp. (° C.)	First slope			Second slope			Transition load (kg./cm ²)
	$B \cdot 10^2$	$\log_e A$	$A \cdot 10^9$	$B \cdot 10^2$	$\log_e A$	$A \cdot 10^{10}$	
19	5.9	-19.64	2.95	7.45	-20.90	8.39	80.3
50	5.7	-18.33	10.95	9.0	-20.53	12.12	65.9
79	6.6	-17.55	23.95	11.1	-19.65	29.38	47.9
102	8.4	-17.43	26.84	13.5	-19.49	34.18	40.2
129	11.1	-17.21	33.46	14.9	-18.68	76.92	35.8
158	11.9	-16.90	45.76	18.7	-18.97	57.99	30.4
182	13.0	-16.25	88.07	27.3	-19.79	25.43	24.6
207	44.8	-18.74	7.29	—	—	—	—

In figure 7 the values of B (for the first and second slopes) are plotted as ordinates against the temperature as abscissae. The resulting curves for each slope are straight

lines, the line for the first slope holding up to the 207° C. value and the second line being true up to the 182° C. value.

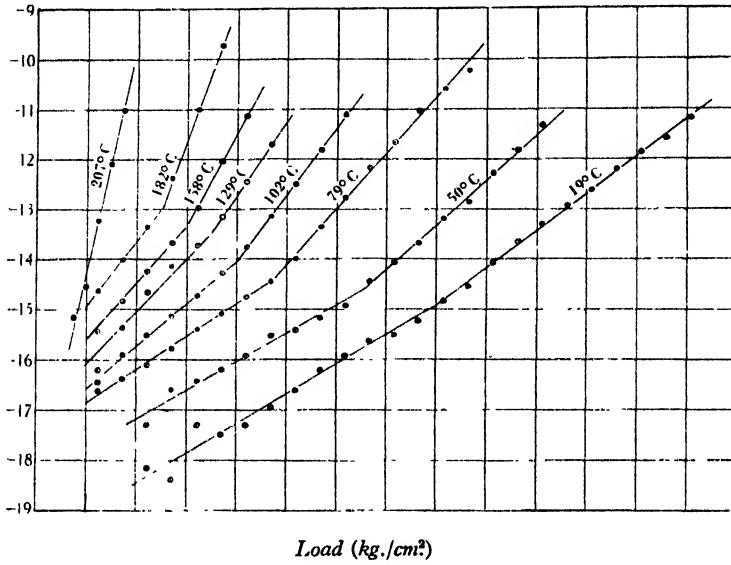


Figure 6. Curves relating $\log_e v$ with load for different temperatures.

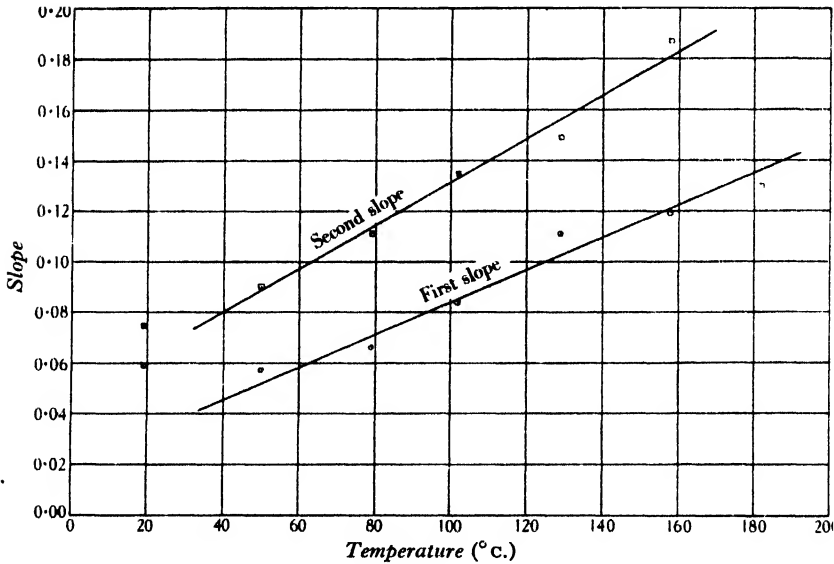


Figure 7. Curves relating the slope B of the $\{\log_e v, P\}$ curves with temperature.

These lines can be represented by the equation

$$B = \alpha + \beta T,$$

where T is the temperature measured in degrees absolute and α and β are constants.

The values of B for 19°C. are considerably off the lines. The allotropic modification from α to β tin occurring at 18°C. (see below) and the consequent doubt as to whether the tin at 19°C. is in the same condition as at the higher temperatures, justifies their omission in evaluating the constants given in table 5.

Table 5

	First slope	Second slope
α	-0.155	-0.187
β	$6.42 \cdot 10^{-4}$	$8.54 \cdot 10^{-4}$

Hence, designating B_1 and B_2 as the first and second slopes, we have the values

$$B_1 = 6.42 \cdot 10^{-4} - 0.155$$

and

$$B_2 = 8.54 \cdot 10^{-4} - 0.187.$$

A straight-line plot was not obtained between A and T , but on plotting $\log_e A$ against the temperature, a linear relation was found to hold, as shown in figure 8.

The 19°C. point was considerably off the first slope line and was again neglected. The corresponding point on the second slope line was well on the curve and included in the evaluation of the constants in the equation

$$\log_e A = \gamma T + \log_e \delta$$

given in table 6.

Table 6

	First slope	Second slope
γ	0.0124	0.0164
$\log_e \delta$	-22.126	-25.658
δ	$2.46 \cdot 10^{-10}$	$7.19 \cdot 10^{-12}$

Hence

$$A_1 = 2.46 \cdot 10^{-10} e^{0.0124T}$$

and

$$A_2 = 7.19 \cdot 10^{-12} e^{0.0164T}.$$

Thus the rate of flow taking place on the first series of slopes can be expressed by the formula

$$v_1 = 2.46 \cdot 10^{-10} \cdot e^{0.0124T} \cdot e^{(8.42 \cdot 10^{-4}T - 0.155)P},$$

and on the second series of slopes by

$$v_2 = 7.19 \cdot 10^{-12} \cdot e^{0.0164T} \cdot e^{(8.54 \cdot 10^{-4}T - 0.187)P}.$$

§ 8. THE RELATION BETWEEN THE VELOCITY OF FLOW AND TEMPERATURE

Similarly, an investigation of the velocity of flow at constant pressure-temperature data gave the relationship

$$v = A' e^{B'T}.$$

In figure 9, $\log_e v$ is plotted as ordinate against T as abscissa, a series of straight lines being obtained. As there are many more constant-load curves and correspondingly

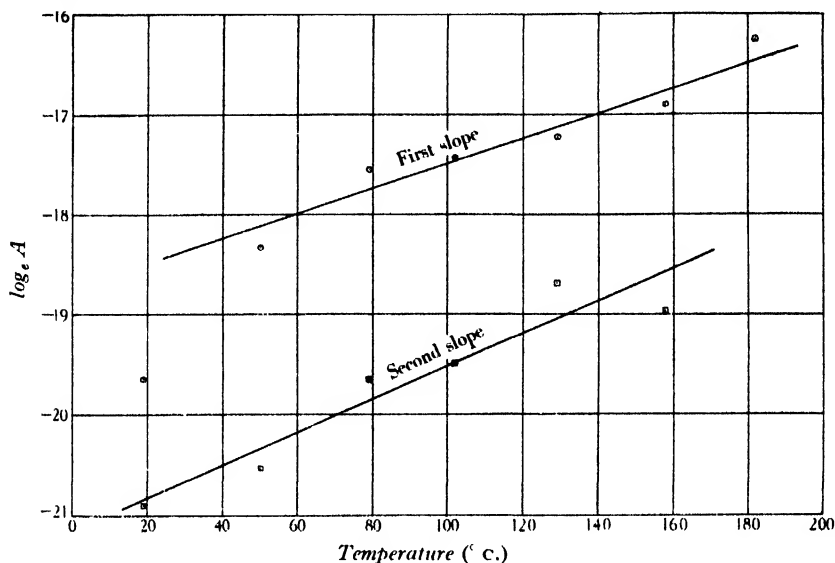


Figure 8. Curves relating the logarithm of the intercept of the $\{\log_e v, P\}$ curves with temperature.

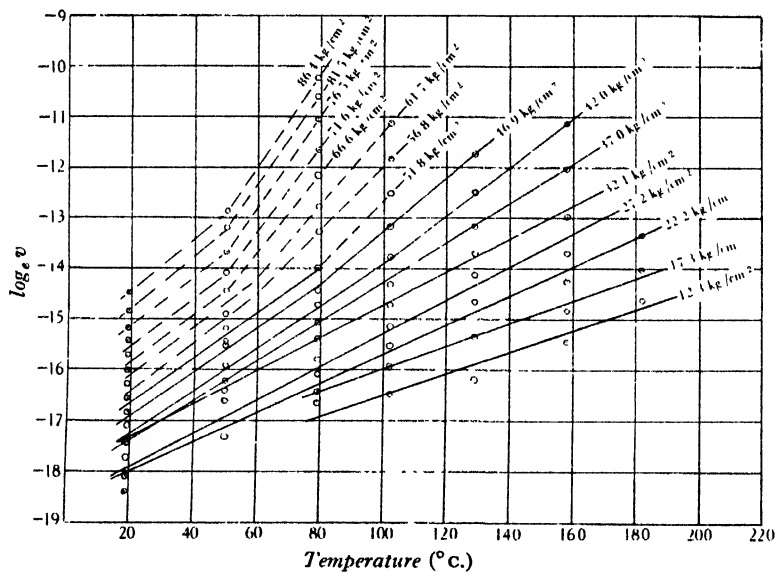


Figure 9. Curves relating $\log_e v$ and temperature for different loads.

fewer points for each curve, the determination of the slope and intercept cannot be made with great accuracy, but yield results of interest. In figure 9 the lines for which there are sufficient data have been drawn in thickly, with dotted lines to indicate the probable path of those curves for which there is inadequate information.

Moreover, for some of the readings taken at the higher temperatures, there is some doubt as to the continuity of the curves owing to the allotropic modification which occurs from β to γ tin. The points at 19° C. for small loads, like the points for the same temperature in figures 7 and 8, lie off their proper curves, but they have not been neglected in this case.

The values of the constants for the second slope corresponding to loads of 56.8 kg./cm.² and upwards can only be considered as indications of the order, being obtained from two points.

In figure 10, values of B' are plotted as ordinates against the corresponding loads as abscissae. It is clear that they fall into two groups, which must be considered as evidence that the $\{\log_e v, T\}$ curves, like the $\{\log_e v, P\}$ curves, change their slope, in this case, at a definite critical temperature—a fact only suggested by the middle-load curves in figure 9. From figure 10 straight-line plots are obtained, the curves representing well the range of slopes whose values it was possible to obtain. If the linear relation is represented by the equation

$$B' = \gamma' + \beta' P,$$

where β' and γ' are constants, the values shown in table 7 are obtained.

Table 7

	First slope	Second slope
β'	$6.77 \cdot 10^{-4}$	$9.91 \cdot 10^{-4}$
γ'	0.0124	0.0104

Hence, if B_1' and B_2' are first and second slopes, they can be written

$$B_1' = 6.77 \cdot 10^{-4} P + 0.0124,$$

$$B_2' = 9.91 \cdot 10^{-4} P + 0.0104.$$

As before, the $\{A', P\}$ plots do not give straight lines, but the linear relation holds for the $\{\log_e A', P\}$ curves, which are given in figure 11, $\log_e A'$ being plotted as ordinate and P as abscissa. The values again divide up into two sets, corresponding to the first and second slopes, and the points lie quite well on the straight lines, which can be represented by the equation

$$\log_e A' = \alpha' P + \log_e \delta',$$

the values of the constants being given in the following table 8.

Table 8

	First slope	Second slope
α'	— 0.164	— 0.242
$\log_e \delta'$	— 22.219	— 23.041
δ'	$2.24 \cdot 10^{-10}$	$9.85 \cdot 10^{-11}$

Hence

$$A_1' = 2.24 \cdot 10^{-10} e^{-0.164P}$$

and

$$A_2' = 9.85 \cdot 10^{-11} e^{-0.242P}.$$

Thus the rate of flow taking place on the first series of slopes can be represented by the formula

$$v_1 = 2.24 \cdot 10^{-10} e^{-0.164P} e^{(8.77 \cdot 10^{-4}P + 0.0124) T},$$

and on the second series of slopes by

$$v_2 = 9.85 \cdot 10^{-11} e^{-0.242P} e^{(9.91 \cdot 10^{-4}P + 0.0104) T}.$$

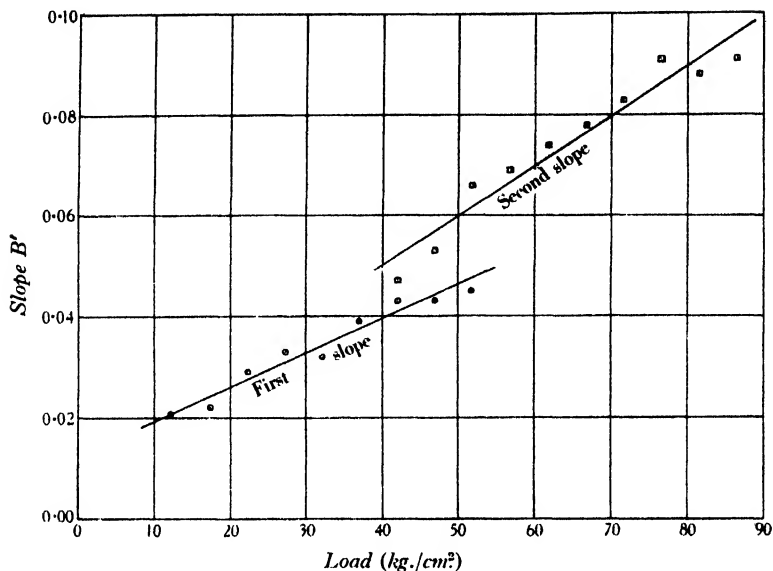


Figure 10. Curves relating the slope B' of the $\{\log_e v, T\}$ curves with load.

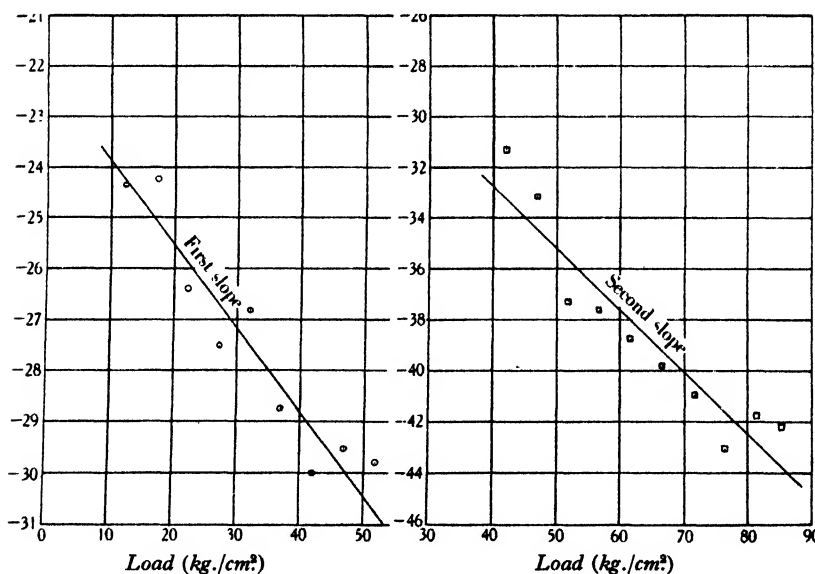


Figure 11. Curves relating the logarithm of the intercept A' of the $\{\log_e v, T\}$ curves with load.

§ 9. EMPIRICAL REPRESENTATION OF RESULTS

Expressions for v have been obtained from both the $\{\log_e v, P\}$ and the $\{\log_e v, T\}$ series of curves and they show, independently, that for any given temperature and load the value of the resulting rate of flow is given by a formula of the type

$$v = \delta e^{\beta PT - \alpha P + \gamma T}.$$

The values of the constants calculated from the different curves are given in table 9.

Table 9

		δ	β	α	γ
First slope	$\{\log_e v, P\}$ curves	$2.46 \cdot 10^{-10}$	$6.42 \cdot 10^{-4}$	0.155	$1.24 \cdot 10^{-2}$
	$\{\log_e v, T\}$ curves	$2.24 \cdot 10^{-10}$	$6.77 \cdot 10^{-4}$	0.164	$1.24 \cdot 10^{-2}$
Second slope	$\{\log_e v, P\}$ curves	$7.19 \cdot 10^{-12}$	$8.54 \cdot 10^{-4}$	0.187	$1.64 \cdot 10^{-2}$
	$\{\log_e v, T\}$ curves	$9.85 \cdot 10^{-11}$	$9.91 \cdot 10^{-4}$	0.242	$1.04 \cdot 10^{-2}$

The agreement between the numerical values of the constants is excellent for the first slope and quite good for the second slope, the values for which cannot be calculated with much accuracy from the available data for the $\{\log_e v, T\}$ curves.

The empirical equation can be written in the form

$$v = K e^{\beta (P+P_0) (T-T_0)},$$

where K , P_0 and T_0 are new constants given by

$$P_0 = \gamma/\beta,$$

$$T_0 = \alpha/\beta,$$

$$K = \delta e^{\alpha\gamma/\beta}.$$

These constants T_0 and P_0 possess a definite physical significance; T_0 is the temperature below which the particular type of flow concerned cannot occur, and P_0 is the corresponding critical load, which, being positive, shows that the temperature is the essential condition for plastic flow, as once the critical value is exceeded, viscous flow will occur for the smallest load applied. It is to be noted that this temperature is below the $\alpha - \beta$ modification temperature, which implies that β tin always satisfies the condition for plastic flow.

These constants, calculated from the values given by the $\{\log_e v, P\}$ curves only, are given in table 10.

Table 10

	P_0 , viz. γ/β (kg./cm ²)	T_0 , viz. α/β	$\beta \cdot 10^4$	$\alpha\gamma/\beta$	$\delta e^{\alpha\gamma/\beta}$
First slope	19.3	241° K.	6.42	2.99	$4.89 \cdot 10^{-9}$
Second slope	19.2	219° K.	8.54	3.59	$2.60 \cdot 10^{-10}$

Hence the empirical equations are, for the first slope

$$v = 4.89 \cdot 10^{-9} \exp \{6.42 \cdot 10^{-4} (P + 19.3) (T - 241)\} \text{ cm./sec. per cm. length,}$$

and for the second slope

$$v = 2.60 \cdot 10^{-10} \exp \{8.54 \cdot 10^{-4} (P + 19.2) (T - 219)\} \text{ cm./sec. per cm. length.}$$

To make v equal to 0 for the critical values the expression must be written

$$v = K \{e^{\beta (P+P_0) (T-T_0)} - 1\},$$

but that this is only a formal requirement is shown by the comparison of certain values of $\exp \{\beta (P + P_0) (T - T_0)\}$ with unity as shown in table 11.

Table 11

P (kg./cm ²)	T (° K.)	$\exp \{\beta (P + P_0) (T - T_0)\}$
0	293	1.9
70	293	2.0 · 10
0	450	1.3 · 10
20	450	2.0 · 10 ²
90	293	1.0 · 10 ³
30	450	1.6 · 10 ⁴

} First slope

} Second slope

This demonstrates clearly that the unity term plays a negligible part for the larger values of P and T . Calculating the rate of flow for $P = 22.2$ kg./cm² and $T = 292^\circ$ K. (the lowest velocity of flow observed) the value

$$v = 1.9 \cdot 10^{-8} \text{ cm./sec. per cm. length}$$

is obtained, when the unity term is neglected, and

$$v = 1.4 \cdot 10^{-8} \text{ cm./sec. per cm. length}$$

when it is taken into account. The difference is $0.5 \cdot 10^{-8}$ cm./sec. per cm. length and as the apparatus is only sensitive to changes per unit length of 4 in 10^6 , there can be no possibility of distinguishing between the two cases.

The experimental results and empirical expressions only hold for tin in the β , tetragonal form, deviations from the relations occurring for the higher temperatures where γ or rhombic tin is being examined.

§ 10. THE ALLOTROPIC MODIFICATION OF TIN

Tin can exist in three allotropic modifications, α (grey) cubic tin, β (white) tetragonal tin, and γ rhombic tin. The temperature at which the change from α to β tin occurs was found by Cohen⁽⁶⁾ to be 18° C. The $\beta \rightarrow \gamma$ modification temperature seems to be known with less certainty; Degens⁽⁷⁾ and Werner⁽⁸⁾ gave 161° C., but Smits and de Leeuw⁽⁹⁾ gave 202.8° C. From experiments on the velocity of effusion at 500 kg./cm² Tammann⁽¹⁰⁾ found a modification point at 203° C. and Jaenecke⁽¹¹⁾, who investigated the modification under pressure, also considered that the value obtained by Degens and Werner was unsuitable.

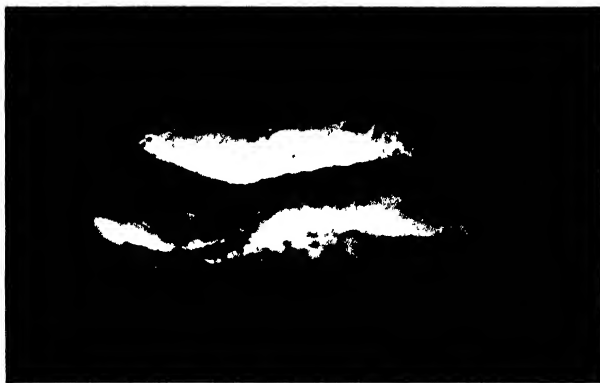


Figure 12*a*. Wire stretched at 182° C.



Figure 12*b*. Wire stretched at 207° C.

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It will be noticed that all the $\{\log_e v, P\}$ curves consist of two intersecting straight lines with the exception of that for 207°C. , which is a single straight line. From the points of intersection it would seem probable that the modification temperature lies between 182°C. and 207°C. A striking confirmation is offered by the examination of the fractures of the wires at these two temperatures. A photograph of the break at 182°C. is given in figure 12*a* on the plate. It shows the twofold nature of the specimen just before fracture and demonstrates that it is due to double glide in two different directions. The specimen at 207°C. , shown in figure 12*b* on the plate, exhibits, however, a clean chisel-like fracture, where glide has obviously been occurring in one direction only. Thus it seems certain that the higher temperature is the true one for the allotropic modification.

§ 11. THE RELATION BETWEEN THE TRANSITION AND BREAKING LOADS AND TEMPERATURE

It has already been noticed that the curves plotted between $\log_e v$ and P and $\log_e v$ and T both change their slope at definite critical values. As the values for the $\{\log_e v, T\}$ curves cannot be considered very reliable, the $\{\log_e v, P\}$ curves have been used to obtain the values of the transition loads and temperatures shown in table 12. In addition, the values of the maximum stress used have been tabulated; these correspond approximately to the breaking load of the wire.

Table 12

Temperature ($^\circ \text{C.}$)	Temperature ($^\circ \text{K.}$)	Transition load P_{12} (kg./cm 2)	Breaking load P_B (kg./cm 2)
19	292	80.3	130.8
50	323	65.9	101.2
79	352	47.9	86.4
102	375	40.2	61.7
129	402	35.8	46.9
158	431	30.4	42.0
182	456	24.6	37.0
207	480	—	17.3

In figure 13 the transition loads P_{12} and breaking loads P_B are plotted as ordinates against the temperatures, in degrees absolute, as abscissae. Both the resulting curves are hyperbolic in form and suggest that

$$(P + P_c)(T - T_c) = C.$$

A point (P_0, T_0) was taken on the curve and the new variables p and t were obtained, where $p = P - P_0$ and $t = T - T_0$, the equation reducing to

$$\frac{t}{p} = -\frac{t}{P_0 + P_c} - \frac{T_0 - T_c}{P_0 + P_c},$$

and t/p can be plotted against t , giving straight-line plots as shown in figure 14. The values of the critical constants P_c and T_c obtained from the slopes and intercepts of

these curves are given in the following table 13, together with the values of the constant C .

Table 13

	P_c (kg./cm ²)	T_c (° K.)	C
Transition-load curve	19.5	161	$1.30 \cdot 10^4$
Breaking-load curve	41.2	174	$2.20 \cdot 10^4$

Hence it is seen that the loads necessary for the transition from the first slope to the second, or for breaking, decrease with increase of temperature in a regular manner.

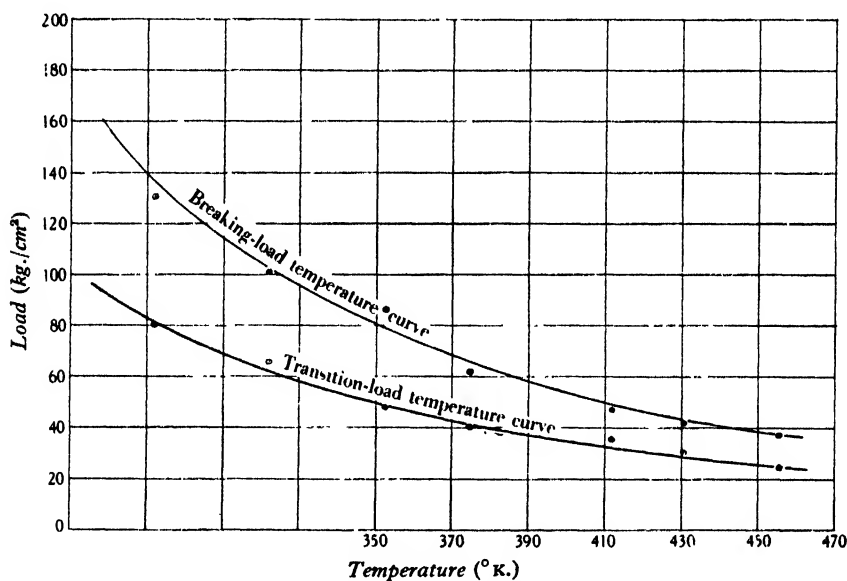


Figure 13. Curves relating critical loads with corresponding temperatures.

The {breaking-load, temperature} curve is in general agreement with the results obtained by Ingall⁽¹²⁾, who has investigated the relation between the tensile strength and temperature for copper, silver, nickel and some alloys. He found that it could be expressed, up to a critical inflection temperature, by a straight line which changes direction at any temperature at which allotropic or phase change may take place, and then, for higher temperatures, by a curved line which may exist in two or more portions. Up to the critical temperature the fracture takes place across both grain and grain boundaries, and there was an indication that above it fracture takes place along the boundaries only.

The curved portion of the curve for higher temperatures represents the stages where breaking is due to gliding along the glide planes of the crystals, the actual fracture occurring at some point where local thinning takes place owing to some fault or irregularity. The hyperbolic relation between the breaking load and temperature for tin has already been given, and the constant T_c , viz. 174°K. ,

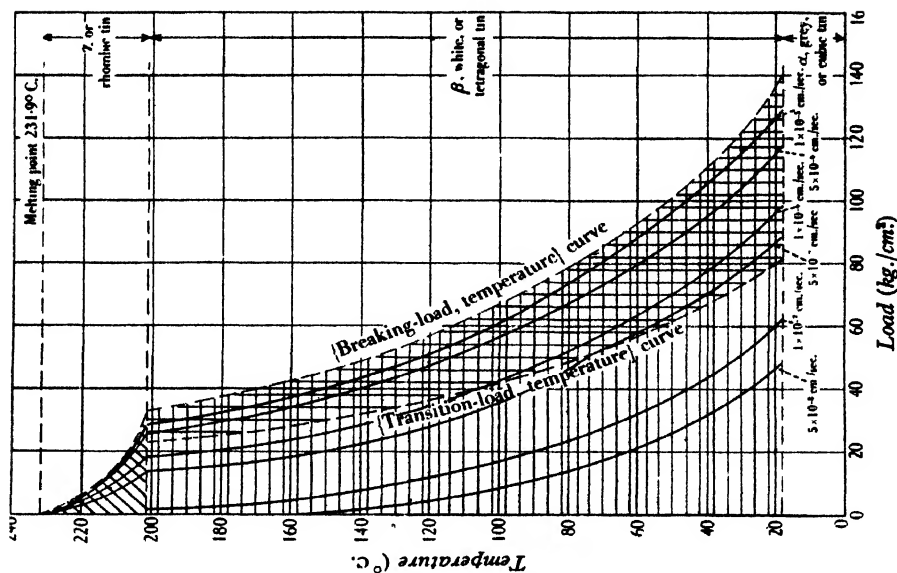


Figure 15. Graphical representation of results.

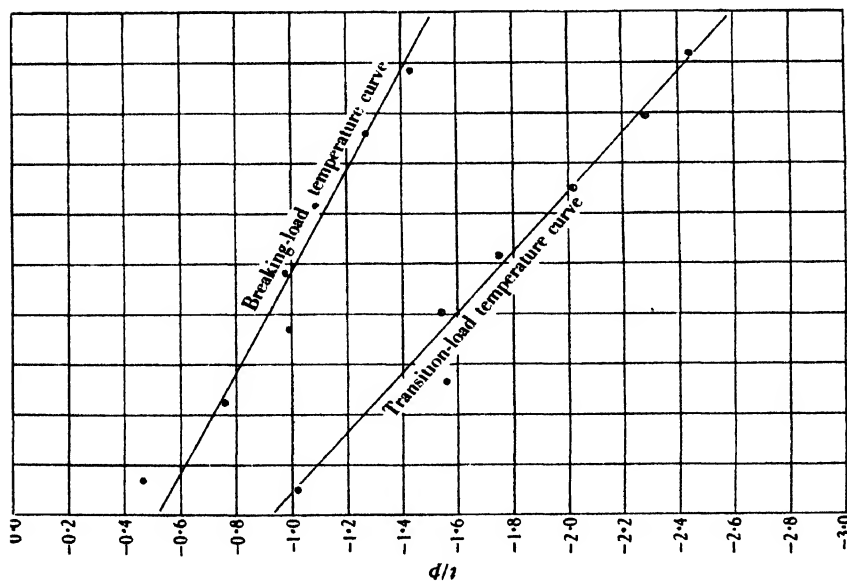


Figure 16. Curves showing t/p with

would give the critical inflection temperature if there were no allotropic modification at 18°C . However, the breaking load must increase with decrease of temperature, until a stage is reached where the load required to cause glide is also large enough to cause fracture across the metal grains, giving the critical inflection temperature and the new stage where the breaking load is connected with the temperature by a linear relation and fracture can occur without glide; a fact that Andrade observed in some experiments on lead at low temperatures.

It is unfortunate that a curve between the least load P_E necessary to start flow and temperature could not be obtained owing to the difficulty of measuring P_E , but it is probable that a similar hyperbolic law would be obeyed.

§ 12. GRAPHICAL REPRESENTATION OF THE RESULTS

The results can be represented qualitatively by the simple graphical representation, shown in figure 15. Loads are plotted as abscissae and temperatures as ordinates, the temperature modifications being indicated by horizontal lines. {Load, temperature} curves are then drawn for certain values of the rate of extension, and are discontinuous at the $\beta \rightarrow \gamma$ tin modification temperature. The {breaking-load, temperature} and {transition-load, temperature} curves are then added as dotted lines. Thus for all points lying above and to the right of the {breaking-load, temperature} curve immediate fracture occurs. The area to the left of the {breaking-load, temperature} curve can be divided up into three portions; (i) the γ tin area, where glide occurs in one direction only, shown by cross-hatching; (ii) the β tin area between the breaking-load and transition-load curves, where glide occurs in two directions, shown by double hatching; and (iii) the β tin area to the left of the {transition-load, temperature} curve, where glide occurs in one direction only, shown by horizontal hatching.

Finally there is the α tin region, which has not fallen within the scope of the present work.

§ 13. THEORY

It has already been stated that when a metal wire is subjected to the necessary load and temperature conditions its extension can be considered to consist of three parts, the elastic extension, an initial extension which dies away with time, and the viscous flow.

It is well known that the viscous or plastic flow is caused by glide of the crystal planes. White tin crystallizes in the tetragonal bipyramidal class, of space group D_{4h}^{19} ; axis $a=5.818\text{ \AA}$. and $c=3.174\text{ \AA}$.⁽¹³⁾, and four atoms are contained in each element. The crystal structure is illustrated in figure 16.

Mark and Polanyi⁽¹⁴⁾ have investigated the extension of single β tin crystals. They found the $[001]$, $[101]$ and $[111]$ directions to be the glide directions and observed that they did not occur with equal frequency. The least usual was $[111]$, which was never found at normal temperatures and only in one case of a wire stretched at high temperature for which the glide occurred in the $[001]$ direction when stretched cold. In each case the glide plane was $\{110\}$. Of the fifteen cases examined, the direction

$[001]$ occurs in eleven, $[101]$ in three and $[111]$ in one only. The glide planes found were the $\{100\}$ and $\{110\}$ planes, the latter being by eight cases to three the more frequent.

The examination of single crystals of β tin was repeated by Obinata and Schmid⁽¹⁵⁾. They confirmed the earlier result that the important translation systems were the $[001]$ direction in either the $\{100\}$ or $\{110\}$ planes. In rare cases, glide was observed in the $[101]$ direction in either the $\{101\}$ or $\{121\}$ planes. These four glide systems were found at each of the temperatures (20° , 100° and 200°) examined, but no evidence of glide in the $[111]$ direction was observed. It is interesting to note that no structural change was indicated by the X-ray photographs taken at 200°C. , which is in line with the conclusion above that the allotropic modification temperature is above 200°C.

This gives a satisfactory explanation of the phenomena observed during the present work. Starting from zero load, any increment will produce elastic extension only until the load exceeds the elastic limit, which is dependent on the temperature, and in some cases is exceeded by the least load applied. When the elastic limit is

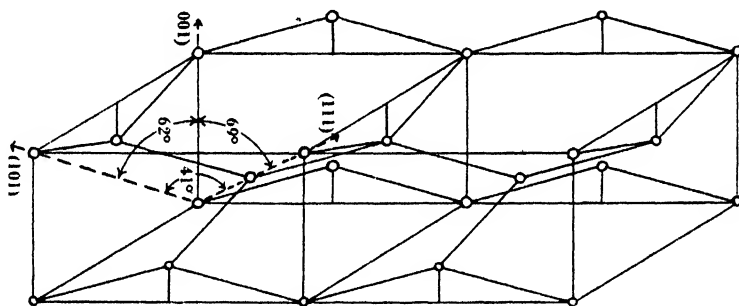


Figure 16. Diagram showing crystal structure of white tin.

exceeded glide occurs along the direction $[001]$, the glide planes being either $\{100\}$ or $\{110\}$, whichever is more favourably oriented to the direction of stress. This continues, the rate of flow increasing with load and temperature as has been described above, until a second critical load temperature condition is reached, when glide occurs in the $[101]$ direction as well, the glide plane being either $\{101\}$ or $\{121\}$ and hence causes the definite large change in the rate of increase of flow with load and temperature as observed.

Now the distance between atoms in the $[001]$ direction is 3.17 \AA. and the angle between the $[001]$ and $[101]$ directions $61^\circ 23'$; hence the distance between atoms in the $[101]$ direction is 6.63 \AA. There is experimental evidence that the direction of greatest atomic density is usually the direction of glide, and it would appear to be safe to generalize that the probability of a direction of glide is a function of the atomic density in that direction. Let us now assume that the flowability in any direction, for given temperature and load conditions, is also proportional to the atomic density in that direction, i.e. inversely proportional to the distance apart of the atoms.

Hence the flowability in the $[001]$ direction can be written as $f(P, T)/d_{[001]}$ and in the $[101]$ direction as $f(P, T)/d_{[101]}$, where $f(P, T)$ is a function of the temperature and load conditions. For single glide the flowability F_s in the direction of load can be written as $k.f(P, T)/d_{[001]}$, where k is a constant depending on the orientation of the $[001]$ direction to the direction of loading.

Taylor⁽¹⁶⁾ has shown that double glide can be expressed as the sum of the separate single glides without simultaneous glide. Thus for double glide the flowability F_d in the direction of loading is

$$k.f(P, T) \left\{ \frac{1}{d_{[001]}} + \frac{\cos 61^\circ}{d_{[101]}} \right\}$$

61° being the angle between the $[001]$ and $[101]$ directions. Hence the ratio of flowability for double and single glide can be expressed as

$$\begin{aligned} \frac{F_d}{F_s} &= \frac{k.f(P, T) \left\{ \frac{1}{d_{[001]}} + \frac{\cos 61^\circ}{d_{[101]}} \right\}}{k.f(P, T) \left\{ \frac{1}{d_{[001]}} \right\}} \\ &= 1 + \frac{d_{[001]}}{d_{[101]}} \cos 61^\circ \\ &= 1.23. \end{aligned}$$

Now the velocity of flow is given by the expression

$$v = \delta e^{\beta PT - \alpha P + \gamma T},$$

and the ratios of the constants α , β and γ taken from the $\{\log_e v, P\}$ curves for double glide (second slope) and single glide (first slope) are given in table 14.

Table 14

	Second slope	First slope	Ratio
	0.187	0.155	1.21
β	$8.54 \cdot 10^{-1}$	$6.42 \cdot 10^{-1}$	1.33
γ	$1.64 \cdot 10^{-2}$	$1.24 \cdot 10^{-2}$	1.32

The agreement of these values with the calculated figure of 1.23 gives support to the hypothesis made above and illustrates the value of single crystal data in the interpretation of results obtained for the behaviour of a mass of crystals in a wire.

§ 14. SUMMARY OF RESULTS

(i) For very small extensions the velocity of viscous flow can be considered to be independent of time, but it is connected with the stretching load by an exponential relation for any given temperature and with the temperature by an exponential relation for any given load.

(ii) The exponential relations

$$v_1 = 2.46 \cdot 10^{-10} e^{0.0124T} e^{(6.42, 10^{-4}T - 0.155) P},$$

$$v_2 = 7.19 \cdot 10^{-12} e^{0.0184T} e^{(8.54, 10^{-4}T - 0.187) P}$$

have been obtained, from the {flow, load} curves, for the rates of flow of tin for glide in one and two directions respectively, and the relation is probably of the form

$$v = K \{e^{\beta (P+P_0) (T-T_0)} - 1\}.$$

(iii) Evidence has been obtained in support of the view that the temperature of the allotropic modification from β to γ tin takes place at 203°C . and not at 161°C .

(iv) The transition and breaking loads have been shown to be connected with the corresponding temperatures by a hyperbolic expression.

(v) The behaviour of the tin wire has been shown to be in general agreement with the results obtained for single crystals.

§ 15. ACKNOWLEDGEMENT

I am indebted to Prof. C. H. Lees for facilities for carrying out this investigation in the Physical Laboratories of Queen Mary College, and for his interest and suggestions during its progress. I desire also to express my thanks for a grant from H.M. Department of Scientific and Industrial Research and to Dr A. D. Crow and the Ordnance Committee for permission to publish this paper.

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DISCUSSION

For discussion see page 311.

AN IMPEDANCE MAGNETOMETER

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ABSTRACT. A magnetometer for measuring local variations of magnetic field uses the fact that the impedance of a nickel-iron wire of high permeability varies with the axial component of the magnetic field in which the wire is placed.

§ 1. GENERAL DESCRIPTION

IT is sometimes desired to effect a magnetic survey of a laboratory, building or locality throughout which the normal magnetic field of the earth is modified by the presence of masses of iron such as girders, water pipes or tanks. The instrument described in this paper has been found very convenient for the purpose, and although it deals with vertical components only it would not be difficult to extend its scope to the measurement of any two horizontal components. The apparatus possesses a wide range of sensitivity and has the advantage that direct readings can be taken as quickly as the instrument can be moved from place to place, without fresh adjustment.

The action of the device depends on the fact that if a high-permeability nickel-iron wire is carrying alternating current its impedance is affected by a change in the axial component of the magnetic field in which the wire is placed^(1,2). Under the correct conditions this change of impedance, which is mainly in the resistance component, may be as large as 20 per cent for a field-change of 0.2 gauss; thus there exists here a relation between field and impedance obviously capable of being used in a practical instrument. In outline, the method of using this relation is to place the nickel-iron wire in one arm of an a.c. bridge which is balanced when the wire is fixed in a constant magnetic field. A change in this field alters the impedance of the wire and upsets the balance of the bridge, producing an alternating current in the detector arm. This current is passed through a low-pass filter to eliminate harmonics, amplified, rectified, and applied to a d.c. microammeter. The output rectification circuit is of special type and enables a central-zero microammeter to be used, increase of field deflecting the pointer to one side of the zero and decrease of field deflecting it to the other side.

Sensitivity can be quickly and easily adjusted between wide limits; for instance between 1000 $\gamma./\mu\text{a.}^*$ and 2 $\gamma./\mu\text{a.}$, although at the highest sensitivities, as is natural, special precautions have to be adopted to achieve reliable readings. In

* 1 $\gamma. = 10^{-5}$ gauss.

fact, at a sensitivity approaching $2 \gamma/\mu\text{a.}$, the instrument becomes suitable only for use at a fixed station for recording variations in the earth's field. The various items forming the complete circuit will now be described in detail.

§ 2. DETAILS OF CONSTRUCTION

The nickel-iron wire. This is of mumetal 26 s.w.g., 9 in. long. It is straightened by passing a current through it when under tension; it is then annealed in hydrogen at 1000°C. for half an hour, and cooled with the furnace. The wire is mounted in a groove on an ebonite strip *a*, figure 1. One end is soldered to a terminal *b* and the other connected to an insulated terminal *c* by means of a small copper spiral. This arrangement has been found necessary in order to avoid setting up strains in the wire.

The wire and its ebonite support, together with the terminals, are mounted on a $\frac{1}{4}$ -in. brass strip *d*, and a cover plate *e* of ebonite serves to protect the wire from injury. The groove is machined in the ebonite base plate so that the wire lies accurately parallel to the sides of the supporting brass block. The whole system is then supported by thread from a point at one end so that the wire hangs

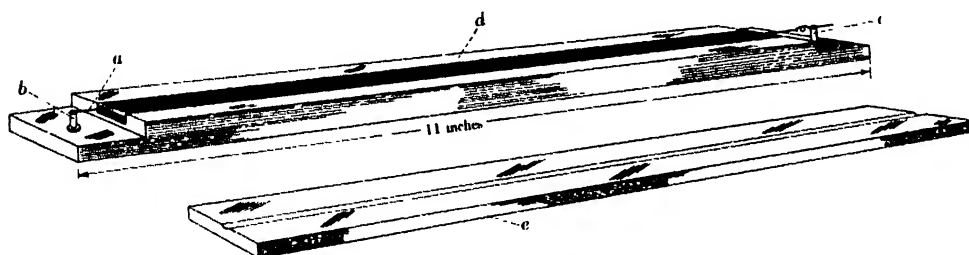


Figure 1.

vertically under gravity. A small bob, not shown in figure 1 but attached to the lower end of the block, dips below the surface of heavy oil in a receptacle suitably mounted, and serves to damp critically the swings of the wire and its mounting when the apparatus is carried from place to place.

The bridge. A Maxwell inductance-resistance bridge having equal ratio arms, is used with the following components; it is shown in figure 2. *a, a* are ratio coils of manganin each of resistance 2.34Ω ., wound non-inductively. *b* is a fixed inductance of about 30 turns of 22 s.w.g. copper wire wound on a paxolin cylinder 5.5 cm. diameter. Its inductance at 500 c./sec. is about $48 \mu\text{H.}$ *c* is the mounted indicating wire of effective resistance 1.1Ω . and inductance $103 \mu\text{H.}$ at 500 c./sec. *d* is a manganin non-inductive resistance for temperature-compensation, of value 0.6Ω . *e* is a variable inductance consisting of two pairs of coils mounted on the ends of two arms rotating on a common axis. The effective resistance of these coils is 0.72Ω . and the inductance can be varied between the limits 99 and $167 \mu\text{H.}$ at 500 c./sec. *f* is a rheostat consisting of a circular bare 16-gauge German silver wire mounted on the rim of an ebonite disk $1\frac{1}{4}$ cm. thick and 15 cm. in radius.

A radial arm carried on a spindle through the centre of the disk makes sliding contact with the circular wire. Resistance can be varied by this means through $0.18\ \Omega$.

It will be realized that this forms a somewhat critical bridge, and in making it up care must be taken to measure and adjust the components accurately before assembly. In order to allow additional latitude for magnetic field much below or much above those for which this bridge is adjusted, three terminals g , h , k , figure 2, are provided, which enable a short length of manganin wire to be inserted in either arm of the bridge. Normally the three terminals are connected by a strip of copper. Since the bridge and, in particular, the nickel-iron wire, possesses a rather large temperature coefficient of effective resistance,* some measure of compensation has been adopted by including a non-inductive manganin coil d in one of the arms.

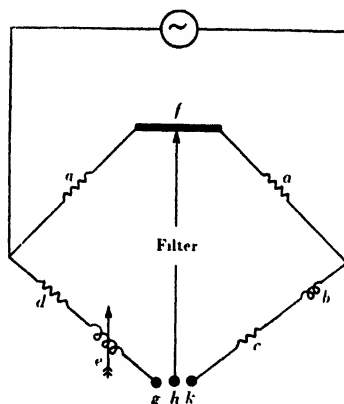


Figure 2.

Further reduction in the effects of temperature has been achieved by mounting the whole bridge in a cork-lagged box which has the additional advantage of forming a very convenient mounting for the nickel-iron wire with its damping system, and for the circular rheostat and the variable inductance. The last two are fitted with spindles and knobs for adjusting purposes, which project outside the lagged box.†

The oscillator. In all measurements involving the peculiar magnetic properties of nickel-iron alloys it is desirable to use alternating current of pure sine-wave form. A simple type of two-valve oscillator working at a fixed frequency is used in the present apparatus. The theoretical diagram is given in figure 3. A tuned anode coil is choke-capacity-coupled in the oscillatory valve circuit and the grid coil is connected via a grid condenser and grid leak. Under these conditions and with a Mullard PM2DX valve with 120 v. anode voltage, the anode current con-

* The coefficient of the nickel-iron decreases as the field increases; typical values are 0.00306 in zero field, 0.00303 in 0.2 gauss and 0.00211 in 1.0 gauss.

† For a periodic temperature wave of amplitude 4°C. and period 12 hr., the time lag produced by the box is about 6 hr.

sumption is less than 1 ma. The anode coil is tuned to 500 c./sec. The output coil also is tuned to the fixed frequency of 500 c./sec. and loosely coupled to the anode and grid coils. This ensures harmonic-free alternating current being fed to the output valve, a Mullard PM2A. The output transformer T of this valve is designed with three output windings. Two are equal in magnitude and supply power at 0.5 v. to the special rectifier-detector which is described below. The third winding supplies 30 ma. to the bridge circuit. The three coils, anode, grid, and output, are enclosed in a sealed tin box in order to be completely screened and prevent pick-up in the bridge amplifier.

The filter. Since the ferromagnetic wire when carrying alternating current will cause harmonics to be generated, it is necessary to connect a suitable filter in the detector arm of the bridge between the bridge and amplifier. In practice the

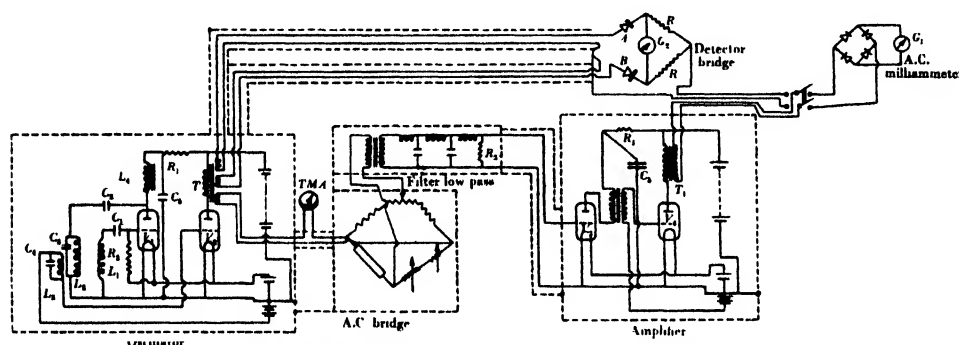


Figure 3. All leads between screened boxes in screened sleeving.

V_1 , PM2DX, V_2 , PM2A, V_3 , PM1A, V_4 , PM2A; L_1 , 6400 turns, L_2 , 6400 turns, L_3 , 5000 turns, on 1-in. inner diameter, 1-in. depth, 36 S.W.G., D.S.C., L_4 , A.F. choke; R_1 , 10,000 Ω , R_2 , 0.5 M Ω , R_3 , 300 Ω , R , 75 Ω ; C_1 , 0.01 μ F., C_2 , 4 μ F., C_3 , 0.05 μ F., C_4 , 0.05 μ F., C_5 , 2 μ F.; T , output transformer of oscillator; T_1 , 13:1 step-down transformer; A , B , Westinghouse 5-ma. CuO rectifiers; TMA , thermal milliammeter; G_2 , d.-c. microammeter.

harmonics generated are of sufficient magnitude to cause overloading of the amplifier. The filter used is of low-pass type and is terminated by a 300- Ω resistance, figure 3. A suitable matching transformer connects the 2- Ω bridge to the filter to match the 300- Ω terminating resistance. The degree of amplification obtainable can be controlled by the step-up ratio of a transformer connecting the filter to the amplifier.

The bridge amplifier. This is a straight two-valve transformer-coupled amplifier using a PM1A valve for the first stage and a PM2A valve for the output stage, figure 3. It is supplied with its own h.t. and l.t. current to prevent interaction with the oscillator. A 3.5 : 1 step-up transformer couples the two stages and the first valve is suitably decoupled by 10,000- Ω anode resistance and 1- μ F. by-pass condenser. The first valve is run at zero grid bias while bias for the output can be supplied either by battery or automatically from a 300- Ω resistance connected in the h.t. negative lead. The output transformer has a 13 : 1 step-down ratio to match the output to the special rectifier detector.

The indicating meters. The output from the amplifier can be measured by one of two alternative methods. The secondary of the output transformer, T_1 , is con-

nected via a double-pole double-throw switch to two different types of measuring instrument. For rough results and to obtain an approximate balance of the a.-c. bridge the output is connected to a commercial rectifier-type a.-c. milliammeter, G_1 , figure 3. This instrument possesses two main disadvantages; it is very insensitive in the zero region, and it will not distinguish between positive and negative outputs from an a.-c. bridge. To overcome these disadvantages, a second type of instrument, the detector bridge described in full below, is connected to the other terminals of the switch and is used in conjunction with a d.-c. central-zero microammeter G_2 . In practice, an approximate balance is first obtained with the a.-c. milliammeter as detector, after which the detector bridge is switched into the circuit for the final balancing operation.

§ 3. THE RECTIFIER DETECTOR BRIDGE

This instrument, which is capable of showing positive and negative changes in impedance, functions on the principle given by C. H. Walter⁽³⁾. The method consists in polarizing the rectifier with a large auxiliary voltage of the same frequency as that supplied to the bridge. Two rectifiers A and B , figure 4 (a), are connected in a rectifier bridge network to which is supplied the small alternating voltage e ; to be measured. At the same time a large auxiliary voltage E is applied to each rectifier from the transformer T , figure 3. The primary of T is fed with alternating current from the oscillator supplying the main bridge, and two secondary

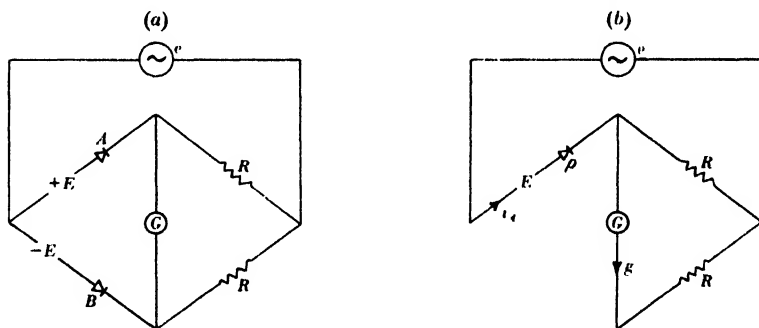


Figure 4. Rectifier detector. e is the out-of-balance e.m.f. from the detector arm of the main bridge. E and $-E$ are the applied polarizing e.m.fs. from windings on the input transformer T .

windings supply voltages in antiphase to the rectifiers A and B . Action is similar to that of the Cosens⁽⁴⁾ a.-c. bridge detector which uses valves instead of copper-oxide rectifiers. Thus a voltage $(E+e)$ acts on one rectifier and a voltage $(-E+e)$ on the other. The corresponding rectified currents pass through two equal resistances R across which a d.-c. ammeter G is connected. Since, for voltages well above the threshold value, the characteristic curve of the rectifier is approximately linear, the current through the meter is proportional to the difference between the amplitudes of the vectors $(E+e)$ and $(-E+e)$.

Referring to figure 4 (a), let E be the voltage applied to rectifier A and $-E$ that applied to rectifier B , and let e be the voltage to be detected.

Assume that a positive half-wave of E is acting in arm A and let i be the instantaneous current in that arm. Since a positive half-wave is in arm A , a negative half-wave of E will be in arm B . But the rectifier B has infinite resistance to negative half-waves. The circuit thus reduces to that of figure 4 (b). Let ρ be the resistance of the rectifier and i_A the current through it. Then

$$i_A = \frac{E + e}{\rho + Z}$$

where Z is the resistance of G and R in series-parallel, so that

$$Z = \frac{R(R+G)}{2R+G}.$$

For the rectifier A let $E = E_0 \sin \omega t$ and $e = e_0 \sin (\omega t + \alpha)$, where α is the phase-difference between E and e . Then

$$i_A = \frac{1}{\rho + Z} [E_0 \sin \omega t + e_0 \sin (\omega t + \alpha)]$$

when $0 < \omega t < \pi$, and $i_A = 0$ when $\pi < \omega t < 2\pi$, since in this case $\rho = \infty$.

Putting I_A for the mean value of i_A over a cycle, and writing $\theta = \omega t$, we have

$$\begin{aligned} I_A &= \frac{1}{2\pi} \left[-\frac{1}{\rho + Z} \right]_0^\pi \{E_0 + e_0 \cos \alpha\} \sin \theta d\theta + \int_0^\pi e_0 \sin \theta \cos \theta d\theta + \int_\pi^{2\pi} (0) d\theta \\ &= \frac{1}{\pi(\rho + Z)} [E_0 + e_0 \cos \alpha]. \end{aligned}$$

Similarly for the mean current I_B of rectifier B , remembering the antiphase sign for E , we have

$$I_B = \frac{1}{\pi(\rho + Z)} [-E_0 + e_0 \cos \alpha].$$

Therefore

$$I_A + I_B = \frac{2e_0 \cos \alpha}{\pi(\rho + Z)} \quad \dots\dots(1).$$

With reference again to figure 4 (a), when the current I_A is flowing in the arm A no current is flowing in the arm B , and vice versa; therefore the total current g in the meter is given by

$$\begin{aligned} g &= \frac{R}{2R+G} (I_A + I_B) \\ &= \frac{2e_0 R \cos \alpha}{\pi(2R+G)(Z+\rho)} = \frac{2e_0 R \cos \alpha}{\pi[\rho(2R+G) + R(R+G)]}. \end{aligned}$$

For g to be a maximum we have $dg/dR = 0$, or

$$[2\pi e_0 \cos \alpha] [\rho(2R+G) + R(R+G)] = [2Re_0 \cos \alpha] \pi(2\rho + 2R + G)$$

giving

$$R = \sqrt{G\rho} \quad \dots\dots(2).$$

It is seen from equation (1) that the difference in amplitude between the vectors $(E+e)$ and $(-E+e)$ is proportional to $2e_0 \cos \alpha$, and this is proportional to the

current through the meter. Thus the deflection of the d.-c. meter G_2 is independent of the magnitude of E , which merely serves to increase the efficiency of the rectifier. Moreover the deflection changes sign when the direction of the voltage e is reversed which is exactly what is required in the present application. The value of R for maximum sensitivity is given by equation (2).

As it is unlikely that two identical rectifiers can be obtained commercially, adjustable resistances must be provided so that zero meter deflection may correspond

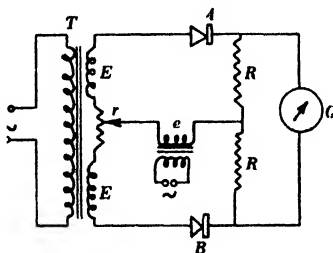


Figure 5.

to zero input in the detecting arm of the main bridge. A simple way of effecting this adjustment is indicated in figure 5, where a variable resistance r , small compared with R , is connected in the circuit as shown. With zero value of the input e , the slider contact of r is adjusted until the meter reads zero.

In the instrument being described the value of ρ was $40\ \Omega$., while G was $140\ \Omega$., so that R is made equal to $\sqrt{(40 \times 140)}$, or $75\ \Omega$.

As has been mentioned on p. 179, the transformer T is supplied with two extra secondary windings having equal numbers of turns such that $E = 0.5\text{ v}$. In the construction of the detector bridge the windings were adjusted to render the use of the resistance r unnecessary.

§ 4. THE INPUT CURRENT

It has been shown^(1,2) that the effective resistance of high-permeability nickel-iron wire varies with the value of the current supplied to the wire and in fact has a maximum value, at any particular frequency, corresponding to a current named the "optimum current". It is clearly of advantage to use this optimum current in the instrument now being described, since not only is the slope of the {resistance, field} curve and therefore the sensitivity greatest under these conditions, but working on the flat maximum ensures that small and unavoidable variations in current shall have the least effect possible on the impedance.

Since the measured optimum current for the wire used, at a frequency of 500 c./sec. is 22 ma., scrutiny of the bridge values given on p. 177 and in figure 2 shows that the input from the oscillator must be kept at 29 ma. This is adjusted on the meter *TMA*, figure 3, by means of a small rheostat not shown in the figure.

§ 5. THE SENSITIVITY OF THE APPARATUS

The sensitivity of the magnetometer is defined as the field-change expressed in gauss for $1 \mu\text{a.}$ on the indicating d.-c. ammeter. To measure this the lagged box containing vertical wire and bridge was placed between two horizontal (Helmholtz) coils sufficiently large to provide a uniform field throughout the space occupied by the wire. The bridge having been balanced by adjustment of f and e , figure 2, a known current is passed in the Helmholtz coils; the deflection on the meter G_2 , figure 3, corresponding to a known field produced by the coils gives the sensitivity of the magnetometer.

For convenience in subsequent use a single coil, of diameter 30 cm. was fixed to the top of the box so that its centre was vertically above the point of suspension of the hanging nickel-iron wire. When a current is passed through this coil the deflection on the meter forms a measure of the sensitivity as determined in the large coils. The scale of the indicating meter was shown to be linear in respect to vertical field by measurements made in the Helmholtz coils.

Sensitivity can be varied by introducing a transformer between filter and amplifier. For the lower sensitivity ranges of the order of $100 \gamma/\mu\text{a.}$ no transformer is used, and this is the arrangement given in figure 3. For higher ranges from $100 \gamma/\mu\text{a.}$ up to 1 or 2 $\gamma/\mu\text{a.}$ transformers of increasing ratio up to 1 : 60 may be used. A certain variation in sensitivity can also be achieved by varying the voltage supplied to the amplifier.

§ 6. ASSEMBLY FOR A SURVEY

For use during a magnetic survey, the box containing bridge and hanging wire is mounted, together with filter, amplifier unit and batteries on a wooden stretcher which may conveniently be provided with non-magnetic tyred wheels. Alternatively,

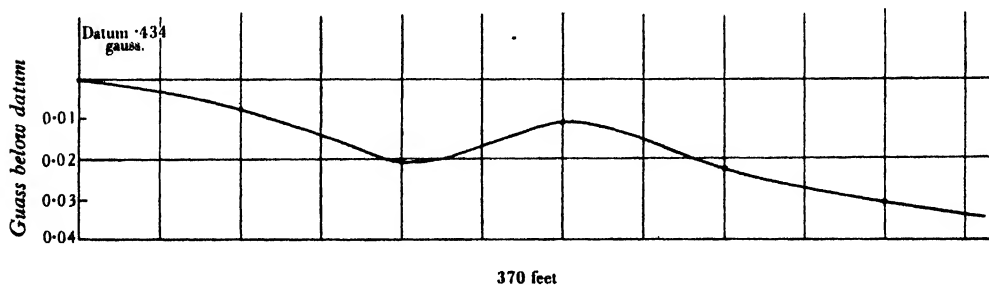


Figure 6. Survey of vertical force.

the stretcher fitted with legs may be carried from place to place by two bearers. Owing to the critical damping of the hanging wire, readings of the microammeter may be taken as quickly as 1 or 2 sec. after the stretcher has been set down. If the optimum current is maintained, sensitivity does not change; it may, however, readily be checked at any time by means of the auxiliary calibrating coil.

The result of a survey of vertical field made with this instrument is given in figure 6 as an example. The region explored contained large masses of iron scattered about at various distances from the line of survey and readings were taken to the nearest $2 \mu\text{a}$, which was equivalent to 100γ . This line was independently surveyed by a different method on a different day and the results of the two surveys agreed to 0.5 per cent.

The impedance instrument was taken four or five times over the line of survey and always returned to its zero reading at the selected datum point. The readings along the line were in agreement among themselves within $\pm 100 \gamma$.

§ 7. ACKNOWLEDGEMENTS

Our thanks are due to Dr J. H. Powell for taking the survey shown in figure 6, and to Mr W. Day and Mr Cousins for valuable assistance during the construction of the instrument. We are indebted to the Admiralty for permission to publish this paper.

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THE APPLICATION OF THE ABSORPTION METHOD TO THE DETERMINATION OF THE UPPER LIMITS OF CONTINUOUS β -RAY SPECTRA

By E. E. WIDDOWSON AND F. C. CHAMPION

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ABSTRACT. (1) An objective method of treating absorption data is devised for obtaining the most reliable value for the upper limit of continuous β -ray spectra. (2) The effect of geometrical conditions, of change of source-intensity, and of source-thickness on the absorption curve and on the apparent upper limit is discussed. (3) Feather's empirical equation connecting range and energy of β rays is corrected in accordance with more recent determinations. The corrected equation is $R = 0.536E - 0.165$. (4) The method is applied to absorption curves obtained for the β rays emitted from Mg^{27} , Si^{31} and As^{76} . The values 0.885 ± 0.068 g./cm.², 0.571 ± 0.047 g./cm.² and 1.400 ± 0.024 g./cm.² are in good agreement with the values obtained by other methods.

§ 1. INTRODUCTION

THE absorption method for the determination of the upper limit of continuous β -ray spectra has the advantages of being rapid and experimentally simple, and of permitting the use of fairly weak sources. Unlike the methods of magnetic focusing and of the expansion chamber, the absorption method gives little information concerning the spectrum itself; but for the naturally occurring radioactive elements it has been found to give satisfactory values of the upper limit^(1,2). The intensities of induced radioactive elements formed with the aid of naturally occurring radioactive elements are usually extremely small. Doubt has been expressed as to the validity of the results obtained by the absorption method for such weak sources, and several workers have noticed that it appears to give low values for the upper limits⁽³⁾.

The object of the present investigation was to devise a method of treating absorption data which would give the most reliable value of the upper limit obtainable from them, and to test the method on various β -ray spectra. The method was applied to results obtained with radium E and with thorium C and found to give values for the end points agreeing with the average values of recent determinations by other methods. The β -ray spectra of Mg^{27} , Si^{31} and As^{76} were next examined and the method was again shown to be satisfactory.

It is interesting to examine the application of the expansion chamber method to a typical source such as Si^{31} which was used in the present absorption experiments. If a standard expansion chamber had been used under conditions conducive to the production of reliable β -ray tracks⁽⁴⁾, then allowing for the decay of the

source, about 1000 photographs would have been required for a reasonable chance of observing a single track. Assuming that photographs may be obtained at the rate of one per minute, this would occupy about 15 hr. The present work on Si^{31} , carried out by the absorption method, occupied about 80 hr. Hence by applying the expansion chamber to sources of the same strength for the same time, a total of six tracks would have been obtained. It would clearly be impossible to deduce an end point from such limited data, whereas the value for the end point obtained from the absorption data in this case is accurate to ± 10 per cent. An increase in the strength of the source, while increasing the efficiency of the cloud-chamber work, would also be accompanied by an increase in the accuracy of the value obtained had the absorption method been used. The general conclusion is that, provided an absorption apparatus has been carefully calibrated in the manner described later, the value obtained for the end point is at least as good as that obtained by a reasonable number of expansion-chamber photographs.

§ 2. DETERMINATION OF THE UPPER LIMIT FROM THE ABSORPTION CURVE

The absorption curve of the β rays emitted from a radioactive substance represents very approximately the integral of the spectrum from the high-energy end. This is by no means accurately true, so the spectrum itself cannot be obtained by differentiating the absorption curve. Both curves, however, approach the energy axis tangentially at the upper limit, although the straggling which results from the absorption process produces a more marked tailing off in the case of the absorption curve. With weak sources, such as occur with induced radioactive elements, this tailing off is increased, for to obtain sufficient intensity (1) a large solid angle must be subtended at the source by the detector, whereupon an exceptionally large proportion of the β particles fail to traverse the absorbing foils in an approximately normal direction; and (2) the source itself must be of considerable thickness. Neither of these factors is at all appreciable under conditions commonly used hitherto, that is, with small surface deposits of naturally occurring radioactive elements and flat absorbing foils.

The usual procedure for determining the upper limit from the absorption curve has been to plot the relative ionization or number of counts against thickness of absorber. The limit is then taken as the range corresponding to the point at which the curve becomes flat as estimated by eye. With strong sources subtending a small solid angle at the detector, the uncertainty introduced by visual estimation may not be large, but this method must always be subjective, and no reliable estimate of the error involved can be obtained. In cases where the weakness of the source introduces large statistical errors, the visual method is much less satisfactory. A visual estimate of the upper limit from absorption curves obtained with weak sources under the present experimental conditions gave results which were far too low.

An alternative method which has been used by some workers is to plot the logarithm of the intensity against the thickness of the absorber and to take as the

upper limit the thickness at which the resulting linear curve cuts the ordinate corresponding to the natural leak or background of the measuring-apparatus. Now it is clear that for β particles which themselves possess a finite upper energy limit, there must be a corresponding upper limit to the absorption curve. This curve, therefore, should not be represented by an exponential function which approaches the range-axis OX asymptotically and which has no finite upper limit.

On the other hand, a curve represented by $y = \sum_n a_n (x_0 - x)^n$, where a_n is a constant and x_0 is the thickness of absorber corresponding to the upper limit, would

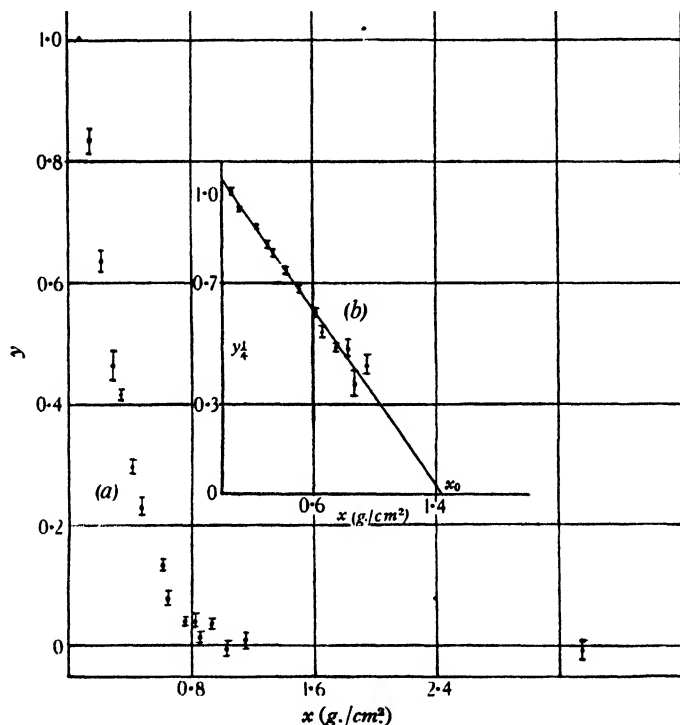


Figure 1 (a) and (b).

appear to be satisfactory. Now the factors producing the absorption curve are very complex, and some empirical expression must be adopted. The present aim is to produce the simplest possible formula which will give a correct value for the end point x_0 . We have found that a single term of the above polynomial is sufficient, the value of n being determined by the type of source and the arrangement of the apparatus. With weak thick sources of radium E, thorium C, Mg^{27} , Si^{31} and As^{76} , separated from the counter by a thin cellophane wall, very nearly the whole range was operative. Under these conditions $n = 4$ gave satisfactory values for the end points. With other radium E sources separated from the counter by a thick glass wall, so that less than one half of the range was operative, $n = 3$ gave more satisfactory results. That a single term in the expression $y = \sum a_n (x_0 - x)^n$ expresses

the experimental results satisfactorily is fortunate, since it allows of a simple calculation of the standard deviations to be made. The latter include, of course, only the errors due to chance fluctuations in the rate of emission of the β particles. Their importance lies in the fact that they give a foundation for comparing the accuracy of different results obtained by the same method. The calculations are carried out in the appendix, pp. 193-5.

As typical of the results, figure 1 (a) shows the absorption curve for As⁷⁶, and figure 1 (b) the corresponding linear relation between $y^{\frac{1}{2}}$ and x . The vertical lines drawn through the points give the values of the standard deviations, and the upper limit is given by the value x_0 where the straight line cuts the X axis.

§ 3. DEPENDENCE OF THE APPARENT UPPER LIMIT ON EXPERIMENTAL CONDITIONS

The dependence of the apparent upper limit on experimental conditions does not affect the result obtained for the upper limit if the value of n for the given apparatus has been found—that is, if the apparatus has been calibrated with the aid of a β -ray emitter whose end point has been determined by some other method. The variation of the apparent upper limit is, however, of a certain general interest and is discussed below.

(a) *Geometrical conditions.* In the present experiments a single-tube counter of aluminium, 0.15 mm. thick, 5 cm. long and 1.5 cm. in diameter was used vertically. The activated sources consisted of concentric cylinders about 2 mm. thick and placed around the counter. The absorbing material, which was in the form of aluminium tubing, could be placed between the counter and the surrounding source. The solid angle subtended by the counter at a point on the source was as large as $4\pi/5$. The straggling of the β particles was therefore very large, and for this reason alone some method other than a visual one was necessary in estimating the upper limit from the absorption curve.

The general results on the dependence of the apparent upper limit on the geometrical conditions agree with those of other workers. Thus Fermi and others⁽⁵⁾, in their preliminary study of β rays from induced radioactive elements, mention that to allow for the geometrical conditions (which were the same as those adopted by the present writers) they applied a correction of about 20 per cent to the apparent values which they found for the mean energy of the β rays. Similarly, Baschwitz⁽⁶⁾ found a variation in the upper limit of radium E when the effective intensity of a source was altered by means of variable apertures in contact with the detecting ionization chamber. On the other hand, no appreciable variation occurred when the aperture was kept constant but different areas of the source were used. It is clear that a large variation is made in the solid angle in the former case but not in the latter.

(b) *Use of a thick source.* Since in order to obtain sufficient intensity the sources of the induced radioactive elements were required in the form of thick cylinders, the calibrating sources of radium E and thorium C were made up in a similar manner. A layer of plaster of Paris about 2 mm. thick, situated between two

concentric cylinders (the outer of ebonite and the inner of thin cellophane), was set with water to which a few drops of an acid solution of radium (D + E + F) or thorium (B + C + etc.) had been added. The three elements Mg^{27} , Si^{31} and As^{76} were produced by neutrons emitted either from a radon-beryllium source of strength up to 60 mC. or from a radium-beryllium source containing 50 mg. of radium in 2-mg. needles. The source and the activated element were surrounded with paraffin wax in the usual manner. To obtain Mg^{27} , aluminium tubes 1 mm. thick were used, while for the production of Si^{31} and As^{76} , amorphous phosphorus and arsenic were used in powder form and contained in hollow cylindrical vessels with inner walls of thin cellophane, leaving a layer of powder about 2 mm. thick. The satisfactory application of a single term with n equal to 4 to the absorption curves obtained with the widely varying radioactive elements examined here would indicate that the sources need be of only approximately the same geometrical thickness. Ideally, for sources to be of the same effective thickness, their actual thicknesses (g./cm^2) would have to be adjusted in accordance with the unknown energy-distribution of their β rays.

(c) *Variation with source intensity.* The sources used in the present experiments varied considerably in intensity from one to another, and it was desirable to examine the effect, if any, of a variation in source-intensity on the apparent value of the upper limit. Measurements were therefore carried out with sources of radium E of different intensities, contained in cylinders with inner walls of glass, but under the previous geometrical conditions. With such sources, only the latter part of the range is operative and it was found that a single term of the absorption formula, corresponding to $n = 3$, gave values for the upper limit in best agreement with the accepted value. The results with four sources of different intensities are shown in table 1.

Table 1

Source	Intensity with 0.275 g./cm ² of absorber	Upper limit (g./cm ²)	Error (standard deviation)
1	101	0.477	0.016
2	58	0.479	0.019
3	11	0.489	0.020
4	1	0.424	0.078

The second column gives the relative intensities of the sources with 0.275 g./cm² of absorber already interposed. The third column contains the corresponding values of the upper limit, while the last column contains a measure of the accuracy expressed in terms of the standard deviation and calculated from the formulae developed in the appendix. It will be observed that, within the limits of error, no consistent variation of the measured upper limit occurs as the intensity of the source is altered. Similar negative results for radium E were obtained by Baschwitz and for Si^{31} by Newson⁽⁷⁾.

§4. RESULTS, AND DISCUSSION OF RESULTS

Our measurements of the absorption of the β particles emitted by radium E, thorium C, Mg^{27} , Si^{31} and As^{76} (two sources) are given in table 2. In column 3, for thorium C, Si^{31} and As^{76} , which have half-value periods of some hours, Y is expressed as the ratio of the number of counts observed to the number which would have been observed had no absorber been present. Expressing Y in this manner as an intensity-ratio allows of the combination of results obtained with sources of different initial intensities. In deducing Y , suitable correction has of course been made for the decay of the source and for the presence of a background count.

For Mg^{27} , which has a half-life of only a few minutes, the intensity-ratio was taken as the ratio of the number of counts with absorber present for the period 1 to 7 minutes to the number of counts without absorber during the period 7.5 to 16.5 minutes. This choice gives an intensity-ratio of about unity for zero absorber.

For radium E, the decay of which was negligible during the time taken by the experiments, the intensity was obtained directly from the number of counts in a given time.

The quantity y plotted in figure 1 is the difference $(Y - Y_0)$, where Y_0 is the effective background count given by the ordinate of the absorption curve after it has become horizontal. These points are discussed more fully in the appendix, pp. 193-5.

In table 3, column 2 contains the values of the upper limits obtained from the intercept on the X axis when $y^{\frac{1}{2}}$ is plotted against x . Column 3 contains the corresponding values of the standard deviations of the upper limits, calculated with the aid of the formulae developed in the appendix. Column 4 gives the percentage value of the standard deviation. In column 5 the upper limits have been converted from g./cm^2 to MV. by making use of Feather's empirical equation⁽¹⁴⁾,

$$R = aE + b, \quad (E > 0.7 \text{ MV.}),$$

where R is the range in g./cm^2 , E is the corresponding energy in MV., and a and b are constants. The equation is based on the maximum ranges and the upper limits of the β -ray spectra of thorium C, radium E and radium C as determined by other methods. A number of recent determinations have been made for radium E; from the mean of the more reliable values*, namely 1.18, a straight line fitted by the method of least squares gives

$$R = 0.536E - 0.165.$$

Upper limits determined directly from the experimental data have been used instead of those obtained from extrapolation of a Konopinski-Uhlenbeck plot⁽²⁰⁾, since the latter usually gives much higher values and it is doubtful if it is a true representation of the spectrum in the region of the upper limit. Columns 6, 7 and 8 contain respectively the values for the upper limits obtained by others, the initials of the corresponding workers and the methods used by them.

Table 2

Source	x (g./cm ²)	Y	Standard deviation of Y
Radium E	0.048	20.70	1.08
	0.119	7.55	0.85
	0.189	1.98	0.58
	0.240	0.61	0.33
	0.309	0.03	0.39
	0.431	-0.57	0.44
	0.517	-0.54	0.39
	0.636	-0.36	0.44
Thorium C	0.815	-0.50	0.38
	0.048	1.000	—
	0.233	0.384	0.0109
	0.306	0.268	0.0067
	0.500	0.070	0.0060
	0.636	0.062	0.0047
	0.760	0.023	0.0019
	0.815	0.021	0.0010
Mg ²⁷	1.548	0.021	0.0014
	0.041	1.092	0.092
	0.081	0.789	0.051
	0.138	0.663	0.029
	0.213	0.411	0.030
	0.281	0.275	0.046
	0.351	0.186	0.026
	0.418	0.086	0.015
Si ³¹	0.473	0.007	0.027
	0.543	-0.019	0.043
	0.632	0.036	0.049
	0.681	-0.004	0.039
	0.797	-0.089	0.087
	1.036	0.007	0.026
	0.051	1.000	—
	0.092	0.862	0.050
As ⁷⁶ (1)	0.119	0.540	0.034
	0.167	0.386	0.023
	0.229	0.178	0.021
	0.292	0.053	0.015
	0.354	0.033	0.018
	0.435	-0.015	0.024
	0.505	-0.012	0.019
	0.600	-0.006	0.023
As ⁷⁶ (2)	0.697	-0.008	0.013
	0.051	1.000	—
	0.119	0.832	0.015
	0.238	0.633	0.012
	0.305	0.462	0.018
	0.354	0.413	0.007
	0.435	0.296	0.006
	0.505	0.221	0.012
As ⁷⁶ (3)	0.613	0.130	0.005
	0.675	0.073	0.003
	0.772	0.047	0.004
	0.841	0.044	0.009
	0.897	0.011	0.003
	0.943	0.029	0.005
	1.033	-0.004	0.007
	1.171	0.006	0.012
As ⁷⁶ (4)	3.3 Pb	-0.006	0.008
	0.048	1.000	—
	0.308	0.460	0.0114
	0.500	0.308	0.0084
	0.636	0.130	0.0057
	0.760	0.008	0.0129
	0.815	-0.018	0.0010
	1.074	-0.018	0.0016
As ⁷⁶ (5)	1.548	-0.013	0.0014

Table 3

Element	Upper limit (g./cm ²)	Standard deviation of limit	Standard deviation (per cent)	Upper limit (MV.)	Upper limit, other workers	Name	Method
Radium E	0.458	0.064	14	1.16	0.475 g./cm ² 1.18 MV.	N. F. ⁽¹⁾ Mean*	Absorption Expansion chamber and magnetic focusing
Thorium C	1.023	0.028	2.8	2.22	0.98 g./cm ² 2.18 MV. 2.25 MV.	J. A. C. ⁽⁸⁾ R. W. G. ⁽⁹⁾ W. J. H. ⁽¹⁰⁾	Absorption Magnetic focusing
Mg ²⁷	0.885	0.065	7.4	1.96	0.95 g./cm ²	M. C. H. ⁽¹¹⁾	Magnetic focusing
Si ³¹	0.571	0.047	8.3	1.37	1.50 MV. 1.44 MV. 1.8 MV.	H. W. N. ⁽⁷⁾ H. W. N. K., R. and P. ⁽¹²⁾	Absorption Weak source
As ⁷⁶ (1)	1.454	0.048	3.3	3.02	3.4 MV. (K-U)	B. and M. ⁽¹³⁾	Expansion chamber
As ⁷⁶ (2)	1.384	0.029	2.2	2.89	2.4 MV. (spectrum ends)	B. and M.	Expansion chamber
As ⁷⁶ (1) and (2)	1.400	0.024	1.7	2.92	—	—	—

Comparing columns 5 and 6, we observe a general agreement between the values for the upper limits obtained by the present method and the mean of the values given by other methods. Considering first the results for radium E, we may note that a very weak source was used, so that the possible error in the upper limit was large. However, within the limits of this error the agreement is quite satisfactory. With thorium C, considerably stronger sources were used and the standard deviation of the upper limit is only about 3 per cent. In spite of the fact that strong γ rays are present and that the spectrum is a composite one, the value for the upper limit agrees well with that given by other workers. Indeed, the method seems to be applicable whether or not γ rays are emitted, for in addition, of the remaining elements, Mg²⁷ and As⁷⁶ emit γ rays while Si³¹ does not.

The agreement shown in columns 5 and 6 for Mg²⁷ is just within the limit of error. It is possible that the true value of the upper limit is slightly below that given by Henderson, who applied the logarithmic method to his absorption data. He had the advantage, however, of a strong source, and small-solid-angle conditions were used.

Several determinations have been made for Si³¹. Thus Kurie, Richardson and Paxton using an expansion chamber found a value 1.85 MV. from their experimental results, although a Konopinski-Uhlenbeck extrapolation gave 2.05 MV. Even the former value is somewhat above the highest value deducible from our results. We find better agreement with the values obtained by Newson, who used the absorption method and two strong sources. The stronger of the two sources gave the higher

* The value used is the mean of the values obtained by Champion⁽⁴⁾, Alichanian⁽¹⁵⁾, Lecoin⁽¹⁶⁾, Lyman⁽¹⁷⁾, Langer and Whitaker⁽¹⁸⁾, and O'Connor⁽¹⁹⁾.

value for the upper limit but no great significance can be attached to the difference as it is almost within his experimental error.

In the present investigation, two determinations have been made for As⁷⁶, one with an earlier apparatus and a background count of 4 per minute and the second with a later apparatus giving a background of 15 per minute. The two results agree well with each other within the experimental error. The mean of the two results is in very satisfactory agreement with the mean of the values obtained by Brown and Mitchell. These workers used an expansion chamber, and two values were obtained by them from experiment and from the Konopinski-Uhlenbeck extrapolation respectively.

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APPENDIX

(1) *Calculation of the upper limit from the absorption curve.* Assuming that

$$y^{\frac{1}{4}} = k(x_0 - x),$$

replace $y^{\frac{1}{4}}$ by z and write $z = h - k(x - \bar{x})$, (i)

so that $x_0 = \bar{x} + \frac{h}{k}$.

Adding n equations of type (i), one for each point to be used in determining the quartic, we obtain

$$S(z) = nh,$$

since $S(x - \bar{x}) = 0$.

Adding the n equations, each multiplied by $(x - \bar{x})$, we have

$$S[z(x - \bar{x})] = -kS(x - \bar{x})^2.$$

Therefore

$$h = S(z)/n,$$

and

$$k = -S[z(x - \bar{x})]/S(x - \bar{x})^2,$$

giving

$$x_0 = \bar{x} - \frac{S(z) \times S(x - \bar{x})^2}{nS[z(x - \bar{x})]}.$$

(2) *Calculation of errors.* We shall assume the following results:

(a) $\text{var } kA = k^2 \text{var } A$, where k is a constant.

(b) $\text{var } \bar{A} = \Sigma (\text{var } A)/n^2$, where the mean \bar{A} is obtained from n values of A .

(c) $\text{var } (A \pm B) = \text{var } A + \text{var } B \pm 2 \text{cov } AB$.

(d) $\text{var } AB = (\bar{A}\bar{B})^2 \left[\frac{\text{var } A}{\bar{A}^2} + \frac{\text{var } B}{\bar{B}^2} + \frac{2 \text{cov } AB}{\bar{A}\bar{B}} \right]$.

(e) $\text{var } \frac{A}{B} = \left(\frac{\bar{A}}{\bar{B}} \right)^2 \left[\frac{\text{var } A}{\bar{A}^2} + \frac{\text{var } B}{\bar{B}^2} - \frac{2 \text{cov } AB}{\bar{A}\bar{B}} \right]$.

(f) $\text{var } f(x) = \left(\frac{df}{dx} \right)^2 \text{var } x$, so that

$$\text{var } A^n = n^2 A^{2(n-1)} \text{var } A.$$

(g) $\text{cov } (A, kA) = k \text{var } A$.

We also assume that the β particles are emitted in a Poisson distribution over successive equal intervals of time, if the source is constant. If the mean number emitted during the interval is m , the probability that x will be emitted is $e^{-m} m^x/x!$, where $x = 0, 1, 2$, etc. For such a distribution the variance is equal to the mean m , and the standard deviation is $m^{1/2}$.

Then if N_1 is the number of counts recorded during a time t with an absorber, b_1 the corresponding background count for time t , and $(N_2 - b_2)$ an estimate of the counts due to the source that would have been recorded in time t with zero absorber, then

$$Y = (N_1 - b_1)/(N_2 - b_2)$$

and

$$\text{var } (N_1 - b_1) = (N_1 + b_1),$$

so that

$$\text{var } Y = Y^2 \left[\frac{N_1 + b_1}{(N_1 - b_1)^2} + \frac{N_2 + b_2}{(N_2 - b_2)^2} \right].$$

The standard deviation of Y , that is $(\text{var } Y)^{1/2}$, for the absorption measurements is given in column 4 of table 2. For radium E, the decay of which is negligible,

$$Y = (N_1 - b_1)/t$$

and

$$\text{var } Y = (N_1 + b_1)/t^2.$$

(3) *Calculation of error in the upper limit.* The value of Y_0 is given by

$$\frac{\Sigma \frac{Y}{\text{var } Y}}{\Sigma \frac{1}{\text{var } Y}},$$

the summation extending over the final horizontal part of the curve. The value of $\text{var } Y_0$ is given by

$$1/\text{var } Y_0 = \Sigma 1/\text{var } Y.$$

Then

$$\text{var } y = \text{var } Y + \text{var } Y_0,$$

and we have

$$\text{var } y^{\frac{1}{2}} = \frac{1}{16} y^{-\frac{1}{2}} (\text{var } y)$$

or

$$\text{var } y^{\frac{1}{2}} = \frac{1}{8} y^{-\frac{1}{2}} (\text{var } y).$$

Finally, having found the value of $\text{var } z$ for each point on the curve, we obtain

$$\begin{aligned} \text{var } x_0 &= \left[\frac{S(x - \bar{x})^2}{n} \right]^2 \text{var} \left[\frac{S(z)}{Sz(x - \bar{x})} \right] \\ &= x_0^2 \left[\frac{\text{var } S(z)}{[S(z)]^2} + \frac{\text{var } S[z(x - \bar{x})]}{[Sz(x - \bar{x})]^2} - \frac{2 \text{cov}\{S(z), Sz(x - \bar{x})\}}{S(z) \times Sz(x - \bar{x})} \right]. \end{aligned}$$

Now

$$\text{var } S(z) = S \text{var } z,$$

$$\text{var } [Sz(x - \bar{x})] = S[(x - \bar{x})^2 \text{var } z],$$

$$\text{cov}\{S(z), Sz(x - \bar{x})\} = S \text{cov}[z, z(x - \bar{x})] = S(x - \bar{x}) \text{var } z.$$

Hence

$$\text{var } x_0 = x_0^2 \left[\frac{S \text{var } z}{[S(z)]^2} + \frac{S[(x - \bar{x})^2 \text{var } z]}{[Sz(x - \bar{x})]^2} - \frac{2S(x - \bar{x}) \text{var } z}{S(z) \times Sz(x - \bar{x})} \right].$$

A NOTE ON THE THEORY OF PHOTOCONDUCTIVITY

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ABSTRACT. It is shown on theoretical grounds that the primary photoelectric current in solids may be expected to tend to zero as the temperature is lowered; the presence of certain kinds of impurity may however prevent this. The theoretical conclusions are compared with the results of experiment.

§ 1. THEORY

ACCORDING to the modern theory of solids the absorption spectrum of a metal consists of broad bands, a conclusion which is in agreement with experiment. For an insulating crystal, on the other hand, so long as the atoms are at rest, the theory leads one to expect a series of sharp lines leading up to a continuous band. The spectrum is thus similar to that of an atom. This was first shown by Peierls⁽¹⁾. According to him the considerable breadth of the absorption bands of thin films observed in, say, the alkali halides⁽²⁾, must be ascribed to the thermal or zero-point vibrations.

The reason for the existence of sharp lines is the following: if an electron is removed from an atom or ion of the lattice, an excess positive charge is left behind; we call this a "positive hole". In the field of this positive hole there will be for the electron a series of stationary states with discrete energy, similar to the stationary states of an electron in the field of a proton. Excitation of the electron into these states will give rise to line absorption; removal of the electron right away from the positive hole will give continuous absorption.

It is clear that absorption of light in one of the sharp lines will not give rise to photoconductivity in the crystal, because the electron is not removed from the field of the corresponding positive charge. One could, however, expect photoconductivity in the region of continuous absorption.

Actually the absorption coefficient in the region of characteristic absorption of, for instance, the alkali halides, is very high, of the order 10^6 cm^{-1} , so that the light cannot penetrate more than about 10^{-6} cm. into the crystal. Experiments on the photoconductivity of, for instance, zinc sulphide or silver bromide are carried out in the long-wave-length tail of the absorption band, where the absorption coefficient is much less than this; in this region we must assume that only a small fraction of the total number of atoms is able to take part in the absorption. These may be atoms at the surface of cracks; for polar salts Herzfeld⁽³⁾ has shown that the work necessary to excite an electron is less at the surface of a crack than for ions in the body of the crystal. They may also be impurity atoms in solid solution.

In the work of Pohl⁽²⁾ and his school on coloured alkali-halide crystals, it is probable that an electron replacing a negative ion in the lattice is responsible for the absorption.

The same conclusion holds for the absorption as before; a line absorption, corresponding to transitions in which the electron is not separated from its positive charge, will lie to the long-wave-length side of the absorption band which corresponds to a freeing of the electron. Such a line absorption is, for instance, observed⁽⁴⁾ in potassium iodide containing traces of silver iodide. In the case of absorption due to random impurities and cracks, we should expect a continuous band made up of a series of fairly sharp lines superimposed. As regards photo-conductivity, however, the same conclusion holds; that in the long-wave-length edge of the absorption band the light cannot release electrons directly.

It is of course possible that the thermal agitation of the lattice may remove the excited electron from the neighbourhood of the corresponding positive charge before it has time to fall back into the normal state. Suppose that the work necessary to free the electron from the excited state is W ; then the probability per time dt that an electron will be released may be taken to be

$$B e^{-W/kT} dt,$$

with B of the order of magnitude of the frequency of the atomic vibrations, and thus about $5 \cdot 10^{12} \text{ sec}^{-1}$. The probability per time dt that an excited electron will drop back to the normal state may be written

$$A dt$$

with A of the order 10^8 sec^{-1} . Then the probability η that an electron will escape from its positive hole before it drops back into its original state is given by

$$\eta = \frac{1}{1 + (A/B) e^{W/kT}}.$$

This function is plotted against temperature in the figure, and is seen to drop rapidly with decreasing temperature.

If $A/B = 2 \times 10^{-5}$, the drop takes place at a temperature

$$\frac{W}{k} / \log_e (5 \times 10^4), \text{ which } \doteq 0.09 W/k.$$

Thus if the drop takes place at room temperature, W will be about $\frac{1}{4} \text{ ev}$.

In any experiment which measures the primary photoelectric current, the current will be proportional to η . We thus reach the conclusion that, when illumination is towards the red end of the absorption region, the current per absorbed quantum must always tend to zero as the temperature is lowered.

This conclusion can be avoided in one case. It may be that all or part of the absorption investigated is due to negatively charged impurities, that is to say, to extra electrons trapped in the lattice in some way, and contributing an excess negative charge to their immediate neighbourhood. In that case no positive hole is formed when the electron is freed, and possibly no stationary state exists except the

normal one, as in the hydrogen negative ion. Then illumination at the red end of the spectrum will excite the electron directly into the conduction band, so that it is free to move away.

For polar crystals this conclusion must be accepted with some reserve, for a reason similar to that discussed by Gurney and Mott⁽⁵⁾ in a recent paper. In order to simplify the discussion let us consider a polar crystal in which the dielectric constant κ is entirely due to the displacement of the positive and negative ions from their mean positions. At a large distance r from the centre, therefore, the field is $-e/\kappa r^2$, and the polarization

$$P = \frac{1}{4\pi} \left(1 - \frac{1}{\kappa} \right) \frac{e}{r^2};$$

the ions are displaced from their mean positions by distances $\pm P/Ne$, where N is the number of ions per unit volume.

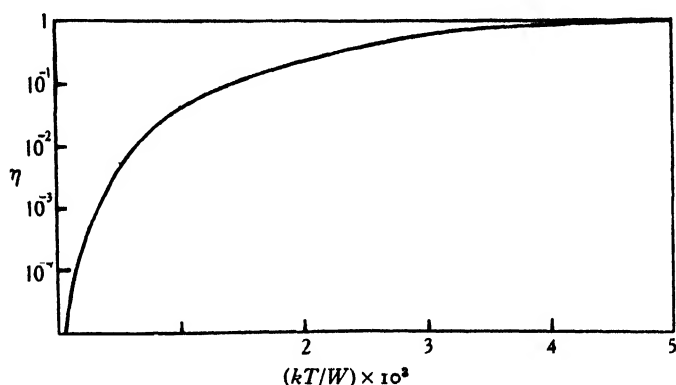


Figure 1. Electrons released per absorbed quantum, as a function of temperature.

Now the time taken by an ion to move from its normal position to its displaced position will be of the order of the period of the residual rays of the crystal, say 10^{-12} sec., which is long compared with the period of visible light. Thus, by the Franck-Condon principle, in considering the optical transitions of an electron trapped at the centre, we must consider the electron as moving in the field due to the ions at rest in their displaced positions. This field near the centre will depend on the structure of the crystal and will not be discussed here; but at large distances r it is simply the difference between the fields e/r^2 in free space and $e/\kappa r^2$ in the medium, and is thus

$$-\frac{e}{r^2} \left(1 - \frac{1}{\kappa} \right).$$

If then we think of the electron as being moved quickly away from the centre, it will find itself in a field of potential energy

$$-\frac{e^2}{r} \left(1 - \frac{1}{\kappa} \right) \dots\dots(1).$$

This is of the same form as the field due to a positive charge, and there will therefore be excited states for an electron in this field. Hence in this case also illumination in the long-wave limit of the absorption band does not free an electron directly.

On the other hand the field represented by equation (1) is due entirely to the distortion of the lattice by the electron; in a time of the order of 10^{-12} sec. after the electron is excited, the neighbouring ions will move into new positions of equilibrium. It is possible that the heat released in this process is enough to release the electron from the centre where it is trapped. In what follows we shall see that there is some evidence that electrons can in fact be released from negatively charged centres at low temperatures.

Finally, we must add that if electrons are released from colloidal particles of metal, we do not expect any temperature dependence of η (cf. Pohl⁽²⁾, p. 20).

§ 2. COMPARISON WITH EXPERIMENT

Alkali halides. Photoconductivity has been investigated mainly in crystals containing F centres. An F centre is probably an electron replacing a halogen negative ion in the lattice; a neighbourhood including an F centre is thus electrically neutral. We expect, therefore, a sharp drop in the photoconductivity as the temperature is lowered below a certain point. Such a drop, by a factor at least 10^3 , is observed at about -150°C. in potassium chloride for example⁽²⁾.

Electrons released from F centres are trapped again to form F' centres, a second type of centre having an absorption spectrum further in the red. The quantum yield of the transition $F \rightarrow F'$ shows, as we should expect, the same temperature dependence as the primary photoelectric current⁽²⁾. According to Pohl an F' centre is an electron trapped at a point where there is already an F centre, in other words two electrons replacing a negative ion; it is therefore negatively charged. We are thus able to understand the fact reported by Pohl⁽²⁾ that as the temperature is lowered the quantum yield of the transition $F' \rightarrow F$ retains its initial value.

Silver halides. Silver bromide is normally an insulator at low temperatures. If it is irradiated with 10^{12} quanta per cm^3 , it afterwards shows electronic conductivity in the dark like a semi-conductor. This excited state is destroyed by high temperatures.

In discussing photoconductivity of silver salts, then, we must distinguish between, on the one hand, ions on the surface of cracks, etc., which give electrically neutral centres from which an electron can be released, and metastable centres where an electron is trapped in some way, giving presumably negatively charged centres.

Photoconductivity in silver halides has been investigated by Toy and Harrison⁽⁶⁾. In annealed crystals they found, as we expect, a marked drop in the current as the temperature is lowered to liquid air temperature. In unannealed crystals no drop was found, and the results obtained were not reproducible. This may be due to electrons in the negatively charged metastable positions.

These ideas may be applied to some recent results of Berg and Mendelssohn⁽⁷⁾ on the sensitivity of photographic emulsions at liquid hydrogen temperatures. They find that the sensitivity of a blue-sensitive emulsion drops to 7 per cent of its value

at room temperature, that of a panchromatic emulsion in filtered red light to 0.02 per cent. It is, of course, by no means certain that all of this fall in sensitivity is due to a decrease in the number of electrons released by the light. However, we can only understand the presence of any sensitivity at all at the temperature of liquid hydrogen by postulating that some of the electrons released by the blue light are in negatively charged centres. We can thus understand the much greater drop in the sensitivity of the dye-sensitized emulsion; an electron can only be released from the electrically neutral adsorbed dye molecule with the help of a quantum of radiation.

Results similar to those of Berg and Mendelsohn have been obtained by Ungar⁽⁸⁾ who finds that with many sensitizers (eosin, pinachrom violet) the red sensitivity disappears entirely at -180° . For pinacyanol, on the other hand, the drop is not much greater than for the blue sensitivity.

Other crystals. In both diamond and in zinc blend Lenz⁽⁹⁾ has found a large drop in the photoelectric current between the temperature of the room and that of liquid air. It has, however, been suggested⁽¹⁰⁾ that the drop is due to the setting up of space charge, which should be more stable at low temperatures. Dr A. L. Reimann has, however, informed me that he has carried out experiments in zinc blend by using flash illumination and thus avoiding the setting up of space charge; he has found that the photo-induced current drops by a factor 40 between the temperature of the room and that of liquid air.*

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* I am indebted to Dr Reimann for permission to refer to his unpublished results.

THE SPECTRUM OF MANGANESE HYDRIDE, MnH

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ABSTRACT. A discharge tube suitable for the excitation of band spectra of the hydrides of refractory metals which do not appear well in a vacuum arc, is described. The spectrum of manganese hydride, MnH, is described; bands have been observed in the red, yellow-green, green, blue, and blue-violet regions of the spectrum. Vibrational quantum numbers are assigned to the bands. The spectrum of MnH is briefly discussed in relation to the spectra of CaH, CrH, FeH, CoH, NiH, CuH, and ZnH.

§ 1. INTRODUCTION

IN a previous brief publication⁽¹⁾ we have reported the occurrence of the spectrum of manganese hydride in a high-tension arc in a flame of burning hydrogen, and in a discharge-tube source. We have now greatly improved the design of the discharge tube and have been able to photograph the spectrum under higher dispersion. The present communication describes the new tube and gives a more detailed account of the spectrum.

§ 2. EXPERIMENTAL

The high-tension arc. In our earlier investigations of the spectra of the hydrides of the metals chromium⁽²⁾, manganese, iron, cobalt and nickel⁽³⁾, we used as source a high-tension arc between electrodes of the metal in a flame of hydrogen burning in air. The arc was maintained by a 5000-v. transformer with an output of $7\frac{1}{2}$ kva. The hydrogen was burnt in a Meker burner with all the air-holes closed. A rapid flow of hydrogen from a commercial cylinder was used, the flame being about 10 in. in height. The burner itself served as the lower electrode, the discharge taking place from a piece of the metal, of dimensions about 5 mm. cube, which stood on a graphite cylinder 1 cm. in diameter resting on the grid of the burner; the optimum length of this cylinder varied with the metal in use, being longer for more refractory metals, but was of the order 2 cm. A long graphite rod projecting into the flame from above was used for the upper electrode, the distance between the two electrodes being about 2 cm.

This source proved capable of producing the hydrides of manganese, chromium, cobalt, and nickel, but for high-dispersion photographs exposures of several hours were necessary, during which the source required constant attention and consumed rather a lot of hydrogen. For manganese and nickel the oxide bands lie in

the same region of the spectrum as the hydride bands, and at times these were strongly developed in the outer part of the flame and tended to mask the hydride bands. Moreover, at atmospheric pressure the line spectrum of the metal was rather strongly produced.

We have also tried to obtain the spectra of the hydrides of the transition elements in other sources. The usual type of arc in hydrogen at reduced pressure has proved unsuccessful, the spectrum of nickel hydride failing to appear at all in this source. A hollow cathode of the Schuler type also failed to produce the hydride bands of manganese or nickel, even when run very hot so that the line spectrum of the metal was strongly displayed and the vapour pressure was such that the metal was quickly driven from the cathode.

The necessary conditions for producing the hydride bands strongly appeared to be that there should be a fairly high partial pressure of the metallic vapour mixed with the hydrogen and a high current density of electrons of moderate velocity; in other words, they were essentially positive column conditions. An attempt was therefore made to design a discharge tube which fulfilled these requirements.

The discharge tube. The chief difficulty in using manganese in a discharge tube is the high temperature necessary to produce sufficient vapour pressure of the metal. All materials of which the tube can conveniently be made become too soft at this temperature to withstand evacuation. After various trials the design shown in figure 1(a) was adopted. A wide pyrex tube T , about 70 cm. long and $3\frac{1}{2}$ cm. in external diameter, with a glass window W at one end and fitted with two large aluminium electrodes E_1 , E_2 , formed the main discharge tube, which was capable of carrying a large current. In the middle of this large tube a small quartz tube Q , whose shape is shown in figure 1(b), formed a constriction in the positive column of the discharge. It was supported by two disks of high-melting-point steel which fitted closely to the quartz and also into the large tube; the steel disks were held together by two thin threaded steel rods. The quartz tube was about 6 cm. long and was of 10 mm. internal bore at the ends and from 3 to 5 mm. bore at the constriction. The high current-density of the discharge produced intense local heating and vaporized some of the metal, which was placed in a small depression in the middle of the capillary. The quartz, not having to stand any mechanical strain or maintain the vacuum, could be heated much more strongly than is normally possible with a discharge tube. The metal reacted to some extent with the quartz, but the product of the reaction formed a surface film which protected the rest of the tube for some time; in any case the quartz tube could easily be replaced.

The electrode E_1 , nearer to the window, consisted of a piece of sheet aluminium bent into a cylinder about 10 cm. long and 3 cm. in diameter. It was supported by a steel rod screwed into it, this rod being sheathed by a length of glass tubing which was sealed into a side tube with red sealing wax. Light from the capillary of the quartz tube Q thus passed through the hollow aluminium electrode to the window. The electrode E_2 , at the other end, consisted of a length of aluminium rod supported on a piece of stout tungsten wire sealed through a pyrex tube which passed through a large rubber stopper fitting into the end of the discharge tube; by removing this

stopper the quartz capillary could be slid out and refilled with the metal under investigation. The whole discharge tube was placed in a wooden trough full of water, two lead weights, cast to a suitable shape, being used to sink it. The discharge was maintained by a 5000-v., $7\frac{1}{2}$ -kva. transformer. A slow flow of hydrogen from a commercial cylinder was passed through the tube when in use, this serving to sweep out any impurities baked out of the quartz or metal by the intense heat.

A piece of metallic manganese, in size about 2 mm. cube, was placed in the centre tube. Visual observation showed that the green system of MnH bands previously observed in the flame was strongly developed as soon as the manganese began to vaporize. The current through the tube and the pressure of hydrogen were

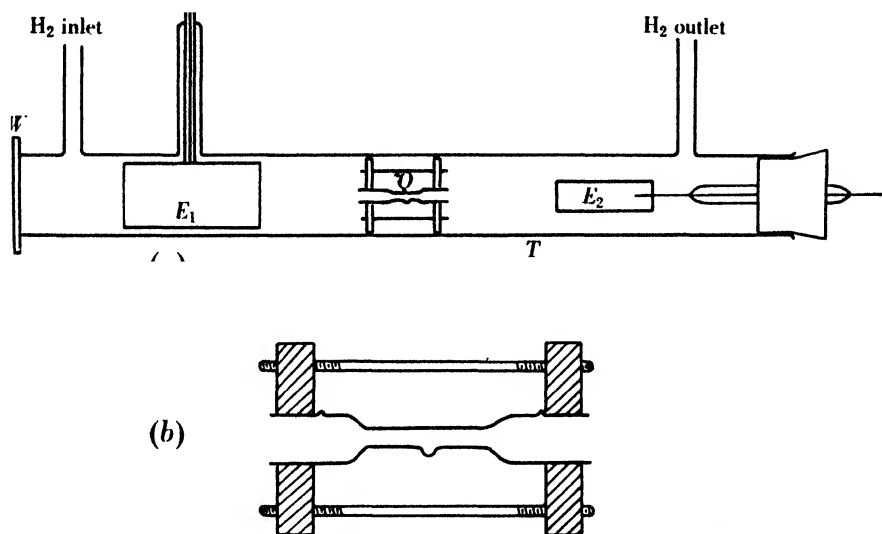


Figure 1. Diagram of the discharge tube. (a) General assembly; (b) central part drawn to larger scale.

regulated so as to bring out the bands as strongly as possible. The pressure of hydrogen was a few millimetres of mercury. As the pressure was raised the potential-drop along the capillary increased, and when this became of the same order as the cathode fall at a steel surface the current passed through the steel frame and formed an additional anode and cathode. At lower pressures the discharge passed through the capillary, which became white-hot. Moderate pressures of hydrogen seemed best for producing the hydride bands, the line spectrum of manganese being brought out strongly if the pressure was too low.

It will be observed that the discharge tube is of robust construction and requires no elaborate glass blowing. All the parts are of simple design and may easily be replaced separately without complete dismantling of the tube. The manganese-hydride spectrum obtained in the tube was photographed in the second order of a 20-ft. concave grating, with dispersion 1.9 Å./mm.; it was found that satisfactory

plates could be obtained in from five to thirty minutes. The tube thus compares very favourably with the high-tension arc, for which exposures of several hours were necessary on the first order of the 20-ft. grating. The spectrum was also much cleaner, being free from oxide bands and showing less continuum at the red end. The secondary spectrum of hydrogen is present on most of our plates but this was not a serious objection for work at high dispersion. These lines could easily be identified by a comparison spectrum; they declare their origin, moreover, by their lack of sharpness due to Doppler broadening.

§ 3. DESCRIPTION OF THE SPECTRUM

We have observed several bands both in the high-tension arc and in the discharge tube. Some of these bands have already been observed by T. Heimer⁽⁴⁾ in emission and absorption and are undoubtedly due to manganese hydride, MnH.

The strongest band is in the yellow-green. It is degraded to the violet and shows a strong head at $\lambda 5677$ and a weaker head at $\lambda 5720$. It is accompanied by two weaker bands of similar appearance, one in the blue-green and one in the red. These bands are almost certainly the (0, 0), (1, 0) and (0, 1) bands respectively of the same system. On account of the complex rotational structure, the heads are difficult to locate exactly, but the wave-lengths and wave-numbers of the stronger heads of the three bands are given in table 1:

Table 1

Band	λ	ν
Blue-green	5172	19330
Yellow-green	5677	17610
Red	6237	16030

These values give the vibrational frequencies, ω_0' and ω_0'' , for the initial and final electronic states as 1720 and 1580 cm^{-1} . Values of these constants for neighbouring elements of the periodic table are presented together in table 2 for comparison:

Table 2

Hydride	ω_0'	ω_0''
CaH ⁽⁵⁾	1333	1299
MnH	1720	1580
NiH	1493	(1900)*
CuH ⁽⁶⁾	1611	1866
ZnH ⁽⁷⁾	1824†	1552
ZnH ⁺⁽⁸⁾	1337	1832

* Calculated from the molecular constants B and D . † Own measurements from heads.

There is also a strong band in the blue. This is degraded to the red and shows heads at $\lambda 4741$ and $\lambda 4794$; it is presumably the (0, 0) band of another system. Five strong branches stretch towards the red from this band, and have a spacing

which suggests that they are of *P* form. The appearance of the band strongly suggests the presence of *Q* branches, and from the occurrence of the five *P* branches it seems that the electronic states involved probably have a multiplicity of five. Until the rotational analysis is complete it is impossible to state the electronic transition definitely, but it is quite likely to be either ${}^5\Pi \rightarrow {}^5\Sigma$ or ${}^5\Sigma \rightarrow {}^5\Pi$. We have already⁽²⁾ briefly discussed the likely electronic states of MnH and either of these transitions seems quite probable on a priori grounds.

There is also a much more open type of band in the blue-violet; the appearance of this structure is best seen from the plate. The band is degraded to the red, but no head has been observed. The strong lines fall into five branches, but these are very erratic and are probably strongly perturbed. These branches close up towards the violet, so that in the region $\lambda 4480$, where they become weak or are absent, the separation between the lines of the same branch is about 16 cm^{-1} , which would seem to indicate that the origin lies in this region. If the strong lines belong to branches of *P* form we should expect to observe *R* branches of approximately the same strength on the other side of the origin. Some strong manganese lines unfortunately make observations difficult in this region, but it is hard to believe that five strong branches do lie here. The band is somewhat of an enigma, but it is hoped that analyses of the other bands may ultimately throw some light on its interpretation.

The rotational structure of all these bands of MnH is of unusual complexity, and if an analysis can be made it should prove to be of unusual interest. It is fairly certain that the blue and blue-violet bands show a multiplicity of five, and the multiplicity of the yellow-green band also appears to be very high; we are thus led to expect many branches of unusual form in addition to the strong *P*, *Q*, and *R* branches.

§ 4. SPECTRA OF HYDRIDES OF RELATED ELEMENTS

Since our discovery of the spectrum of nickel hydride, NiH, in the flame of hydrogen containing nickel carbonyl vapour, spectra of the diatomic hydrides of several related elements have been obtained.

With chromium we have observed a band in the region $\lambda 3600\text{--}3700$ which we attribute to CrH. It was obtained with the high-tension arc-in-flame source described in the introduction. Bands attributed to cobalt hydride have been observed by A. Heimer⁽⁹⁾ at Stockholm. The (0, 0) band is in the region $\lambda 4492$ and is degraded to the red. A band at $\lambda 4288$ attributed to iron hydride, FeH, has also been reported by A. Heimer⁽¹⁰⁾. The band is designated ${}^1\Sigma \rightarrow {}^1\Sigma$ in this report, but this is presumably a misprint, for FeH, having an odd number of electrons, must show an even multiplicity.

These elements of the third period of the periodic table all show roughly the same binding energy and stability when they form diatomic hydrides. These elements, and also zinc in the next row, in their unexcited states all have the electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6 3d^n 4s^2$, where *n* takes the values 0, 4, 5, 6, 7, 8, and 10 for the elements calcium, chromium, manganese, iron, cobalt, nickel, and zinc respectively. The configuration $3d^9 4s^2$ in the series belongs to copper,

but in this case it is not the normal state, for one of the $4s$ electrons falls back into the d shell giving $3d^{10} 4s$; this configuration puts copper with the monovalent elements of group I, but excitation to $3d^9 4s^2$ would bring copper into the series we have been considering and so it should show relationship with iron, cobalt, and nickel. Thus it seems likely that for these elements the binding with the hydrogen atom is due chiefly to the electrons in the $4s$ shell and that the unfilled $3d$ shell is relatively unimportant apart from its effect on the multiplicity of the spectral terms. The molecular constants for some of these hydrides have not been calculated yet, so a quantitative comparison of the binding forces cannot be made at present, but if such a comparison could be made it might well increase our knowledge of the general problem of the binding forces in diatomic molecules.

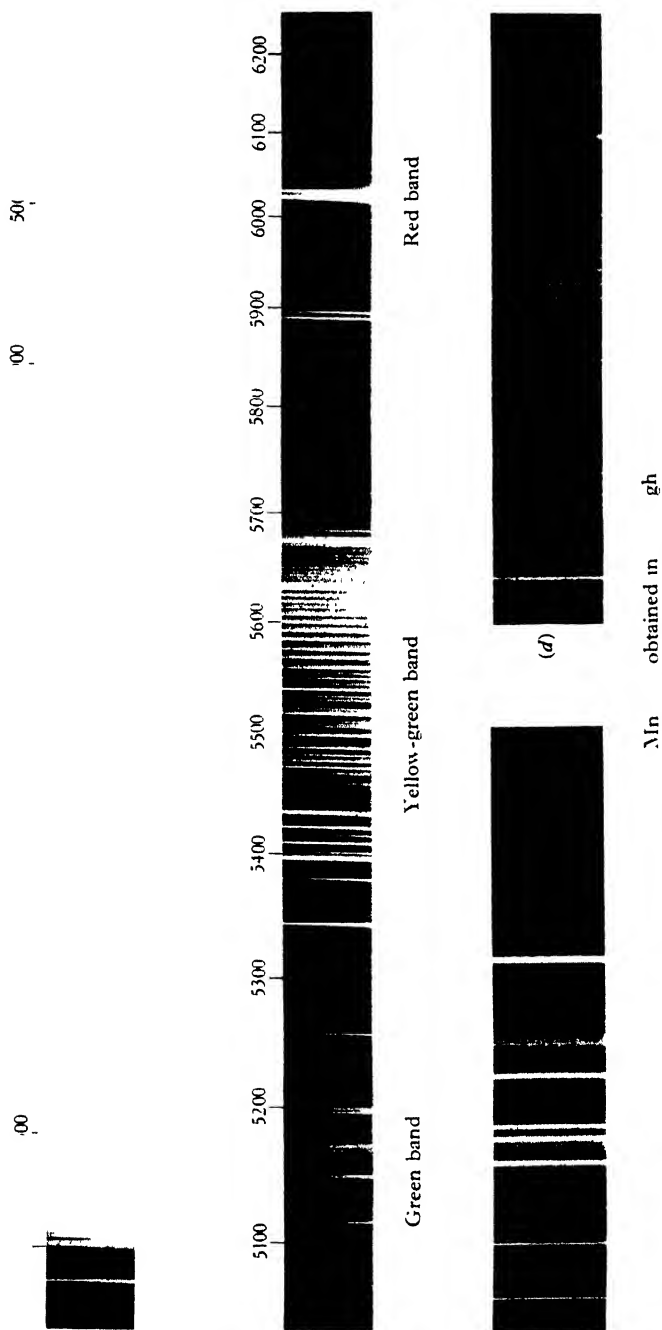
§ 5. DESCRIPTION OF PLATES

Plate 1. (a) and (b) are the spectrum of MnH as obtained in the high-tension arc in hydrogen flame and photographed on a glass prism spectrograph with an exposure of 20 min.; (c) is an enlargement of the blue band of the same spectrum; (d) is an enlargement of the yellow-green band.

Plate 2 shows the spectrum of MnH as obtained in the discharge tube, photographed in the second order of a 20-ft concave grating, with an exposure of 18 min. (a) and (b) are the violet band, and (c), (d) and (e) the blue band. In (e) the five strong branches which are probably of P form are indicated.

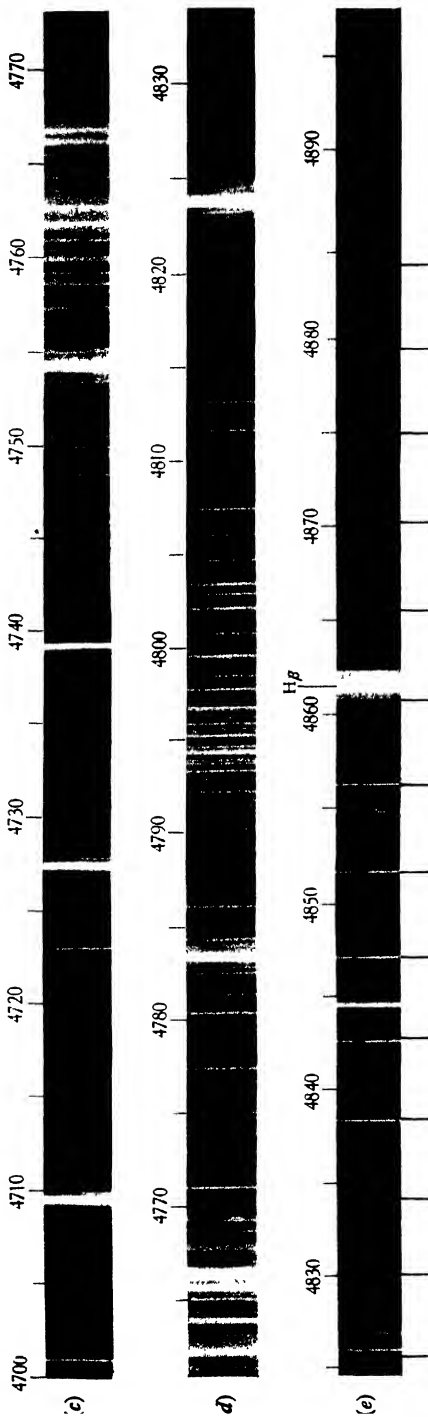
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50
40
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Sp. um of MnH ob ned ub

THE SPARKING POTENTIAL OF MERCURY VAPOUR

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ABSTRACT. The sparking potential of mercury vapour between parallel electrodes previously degassed at about 750°C . was measured throughout a wide range of vapour densities, and the influence of the material of the cathode on the sparking potential was examined. The sparking potential was found to be almost a linear function of pd from about 500 to 5000 v. where p , d are the density of the vapour and the distance between the electrodes, respectively. The minimum sparking potential was measured for a nickel cathode, a steel cathode, and when the cathode was covered with a film of mercury; and the potentials were found to be 400, 380, and 305 v. respectively.

§ 1. INTRODUCTION

THE measurements of the sparking potential of pure monatomic gases is of interest in the general theory of the conduction of electricity in gases owing to the relative simplicity of the molecule in its reaction with the colliding electrons. Further, it appears to be a general rule that, except in the case of helium, the minimum sparking potential increases with the atomic number of the gas, and that the corresponding value of pd decreases, where p is the pressure of the gas and d is the distance between the electrodes. This paper describes experiments carried out with mercury vapour in order to find whether this gas has the same general electrical properties as the noble gases in spite of its lower ionization potential. The measurements were extended to pressures of one atmosphere because high pressure mercury vapour discharges have recently found industrial application. Consequently it is of interest to find whether any change in the nature of the primary ionization process is indicated by the sparking-potential curve. For instance, the presence of minute traces of impurity in certain monatomic gases containing a high concentration of metastable atoms causes marked changes in the slope of the sparking curve when the relative importance of the different processes of ionization changes⁽¹⁾.

Again, if the nature of the cathode surface plays a predominant role in the maintenance of a discharge current however small, whether as a result of the bombardment of positive ions or of metastable atoms or to the incidence of radiation from the current, then the sparking potential will depend on the work function of the cathode surface, and it should have different values with different cathode

surfaces. In many previous investigations, particularly with the permanent gases, the measurements have been found to be almost independent of the nature of the cathode surface, but this conclusion is of doubtful validity owing to the neglect of the complete out-gassing of the cathode. Gas layers on the cathode probably make all metals behave as if they have the same work function, and it is therefore improbable that any difference would be observed for different metals if they had layers of the same gas on their surfaces.

§ 2. DESCRIPTION OF THE APPARATUS

The type of discharge tube used is illustrated in figure 1. The electrodes consisted of disks 3.8 cm. in diameter and about 1 mm. thick, having their edges bevelled to avoid sharp points. One electrode was made of nickel and the other of Staybrite steel. They were highly polished and, together with the tungsten wires for the seals, they were heated in vacuo at a temperature of about 750° C. for many hours before they were fixed in the tube. The distance between the electrodes was 2.55 mm. and the ratio of the diameter to the distance apart was about 15, so that the field between them could be regarded as uniform^(a).

When the tube was complete it was maintained at a temperature of 400° C. for some days while it was continuously evacuated with a diffusion pump and the usual liquid-air traps.

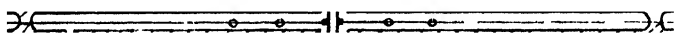


Figure 1.

In order to raise the density of the mercury vapour to any desired value the tube was placed inside an electric furnace. The temperature inside was indicated by a mercury thermometer so placed that its bulb was as near as possible to the electrodes when the discharge tube was in position. The whole of the tube, including the seals, was maintained at the same temperature, while the discharge itself was observed through a window. This was made of steel tube 1 cm. in diameter screwed into the wall of the furnace; and it contained a short glass rod extending perpendicularly from the discharge tube to the outer case of the furnace, and the small space around the rod was tightly packed with asbestos. It was found that this method of conducting the light from the spark involved the minimum cooling of the part of the tube opposite the window.

Up to 500 v. the high-tension supply was derived from a battery of small accumulators, but for higher potentials up to 6000 v. the supply was obtained by rectifying and smoothing adequately the output from a step-up transformer. The potential difference across the electrodes was measured by means of a milliammeter in series with a 4-M Ω resistance, and also by means of an electrostatic voltmeter.

§ 3. EXPERIMENTAL PROCEDURE

In some experiments the spark was detected by an electrometer method in which the total charge passed between the electrodes was exceedingly small, but it was found that the same results were obtained by a simpler method—that of observing the glow when there was a resistance of 16 M Ω . in series with the tube.

The vapour pressures of the mercury at the various temperatures T were obtained from tables⁽³⁾, and the curves were drawn to show the variation of the sparking potential V with the pressure p . Initial experiments revealed that the curves taken while the temperature of the tube was rising did not coincide with those obtained while the temperature was falling. This was due to a small lag between the thermometer reading and the actual temperature of the discharge tube. Thus, when the temperature was rising the thermometer was slightly warmer than the vapour, and when the temperature was falling the thermometer was slightly cooler than the vapour. The method adopted in order to obtain the temperature of the vapour corresponding to the potential V was as follows. It was assumed that the temperature lag was the same whether the tube was warming up or cooling down (and any error introduced in this way is not serious); then for any given sparking potential the corresponding temperature of the vapour was obtained by taking the mean of the two temperatures recorded during the heating and cooling. A very large number of runs were made with many different tubes over a period of some months, and all the results obtained by this method were found to be the same within the experimental error. This was greatest at the highest temperature and it was then about 3 per cent.

§ 4. THE MINIMUM SPARKING POTENTIAL

The measurement of the minimum sparking potential is of interest because in this region any errors in the determination of the gas pressure are of no account, consequently changes in the sparking potential due to changes in the cathode surface are more easily seen. During the preliminary measurements it was noticed that the minimum was about 80 volts lower when the temperature was rising than when it was falling. This difference could not of course be attributed to any change of pressure during the rise and fall of the temperature, and it was found that the lower minimum was the same whatever metal was used as cathode. Further, the difference was only obtained under certain conditions, and those were conditions under which it was expected that mercury would be condensed on the electrodes; for example when the cold tube was heated from room temperature to about 180° C. a film of mercury was seen to condense on the electrodes. On the other hand, when it was certain that the mercury would be all evaporated from the electrode surfaces the lower value of the minimum sparking potential was not obtained. The lowest value of the minimum sparking potential must therefore be attributed to the observed film of mercury condensed on the cathode surface. This film could be removed simply by heating the glass tube near the electrodes with a blow-lamp. Moreover, if the tube was heated first to 360° C. and then allowed to cool to about

180° C. the electrodes were slightly warmer than the glass and no film was observed to condense; the electrodes remained bright. Tubes which had been in use for some time were treated in this way, and the electrodes were also heated by passing a discharge between them before sparking curves in the region of the minimum were

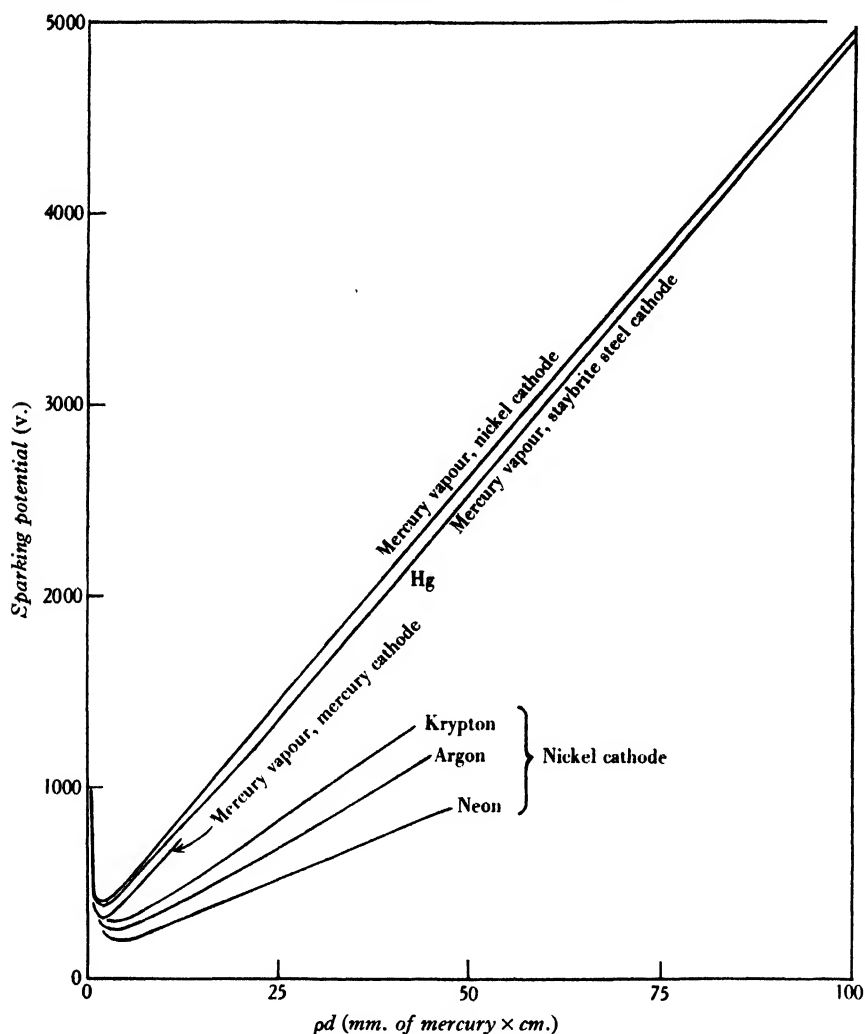


Figure 2.

taken. Further, new tubes were constructed from which all mercury was excluded during the out-gassing process by means of liquid-air traps, and the sparking potentials were measured immediately after the pure mercury had been introduced and the tube sealed off. After a number of measurements made in this way, the highest reproducible value of the minimum sparking potential thus obtained was taken as the value for the clean electrode. These values* were: 400 v. for the nickel

* A preliminary account of these results was published in *Nature*⁽⁴⁾ in December 1936.

cathode, and 380 v. for the Staybrite steel cathode. By warming up the cold discharge tube to about 180° C. the electrodes were covered with a film of mercury, and with each electrode in turn as cathode the minimum sparking potential was found to be 305 v.

§ 5. DISCUSSION OF THE RESULTS

The correct spark parameter is the product of the distance d between the electrodes and the density ρ of the vapour. As the temperature of the vapour rises both the density and the mean energy of agitation of the atoms increases. However, even at 360° C. the mean energy of the atoms is so small compared with that of the electrons that any effect on the ionization can be neglected. The parameter here adopted is the product of d and the pressure p at which a permanent gas at a temperature 15° C. would have the same density as the mercury vapour at a temperature T ° C. This pressure is easily found from the saturation vapour pressure of the mercury by multiplying by $(273 + 15)/(273 + T)$, assuming that association is negligible. This parameter then facilitates comparison of the sparking curves for mercury with those published for the permanent gases. The $V, \rho d$ curves for nickel and steel cathodes are given in figure 2, from which it can be seen that V is practically a linear function of ρd from about 500 to 5000 v. The value of ρd at the minimum was 1.2 while at the highest vapour density used ρd was 100 and V was nearly 5000 v.

For comparison the sparking curves for the noble gases near the minimum potentials are also given in figure 2, and for these we are indebted to Dr S. P. MacCallum. It can then be seen that mercury vapour has the same general sparking characteristics as these gases, in that the minimum sparking potential increases and the corresponding value of ρd decreases as the atomic number of the gas increases; except in the case of helium.

The various values of the minimum sparking potential for mercury show that they are characteristic of the metal of which the cathode is made only if it has been out-gassed. This dependence of the minimum on the cathode surface affords definite evidence in support of the view that the cathode plays an important role as a source of electrons in maintaining a discharge current.

§ 6. ACKNOWLEDGEMENTS

We wish to express our best thanks to the Department of Scientific and Industrial Research for a grant made to one of us (W. R. G.) during these investigations, and to Prof. E. J. Evans for extending to us the facilities of his laboratory.

Note added in proof. Since this paper was communicated, values of the minimum sparking potential of mercury vapour have been published by R. Grigorovici⁽⁵⁾. There is general agreement between his results and ours, but for a clean iron cathode he found a minimum potential of 520 v., and with the cathode covered with mercury a potential of 330 v. was obtained. These compare with the lower values of 380 v.

and 305 v. respectively which were given by us⁽⁴⁾. Grigorovici considered that his higher values were due to the incomplete degassing of the electrodes in his experiments, but it appears to us that the difference might be partly due to nonuniformity of the electric field between those electrodes. It is well known that the sparking potential of the monatomic gases varies considerably with the ratio of the diameter of the electrodes to their distance apart when this ratio is less than 10. If the ratio is too low the sparking potential is raised in order to make good the loss of ionization due to the diffusion of the electrons into weaker parts of the field. Because this diffusion is very marked in monatomic gases the value of 15 was adopted for the ratio in our experiments.

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A NOTE ON NUCLEAR SELECTION RULES

By C. D. ELLIS, F.R.S.

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ABSTRACT. Experiments have been made to determine the intensity of a γ ray of 3.2 MV., suspected to be emitted by ThC'' —Th.Pb, by comparing the number of recoil protons from deuterium with those due to the well known γ ray of 2.62 MV. It appears most probable that between one and three quanta are emitted in every hundred disintegrations. This result is shown to lend support to the view that it is practicable to assign to the various nuclear states experimental spin values which can be used consistently in different sets of selection rules.

§ 1. THE NUCLEAR SELECTION RULES

IN the present state of theory there are two important nuclear selection rules, one governing transitions of an excited nucleus, the other the disintegration of a nucleus with the formation of the product nucleus in one of its excited states. Both of these rules are expressed by assigning spin values to the various states and relating the probability of a given change to, in addition to other factors, the change of spin occurring in the process. The present note deals with the criteria which determine the probability of radiative changes of an excited nucleus. There are good theoretical grounds for considering such changes to be permitted as involve a spin-change of either 1 unit, 2 units, or zero, zero to zero being forbidden. A direct experimental method for determining whether the spin-change is 1 unit (for a dipole transition) or 2 units or zero (for a quadripole transition) is provided by observation of the internal conversion coefficient, which is always greater for a quadripole transition. In this way it is possible to assign a set of relative spins to the various excited states of a nucleus. To take a particular case, the level-system of Th.Pb is shown in the figure⁽¹⁾ with the spin-values, the energies of the states, and the relative excitations that arise from the disintegration $\text{ThC}'' \rightarrow \text{Th.Pb}$. It should be mentioned that these spin-values not only account for the formation and transitions of Th.Pb but also form part of a consistent scheme covering all the four bodies ThC, ThC', ThC'' and Th.Pb. It was a matter therefore of some importance when various workers obtained indications of the emission of a γ ray of about 3.2 MV. corresponding to the transition from the uppermost to the lowest level, since in this case the spin-change of 3 units should forbid the transition or at least make it extremely improbable.

§ 2. PREVIOUS INVESTIGATIONS

The first indications of this γ ray were obtained by Chadwick, Blackett and Occhialini⁽²⁾ when they were investigating with a cloud chamber the production of positron-electron pairs from lead by the γ rays of ThC''. They observed a few

tracks having energy slightly too high to be associated with the main 2.62-MV. γ ray X, but while suggesting the possibility that these were due to the 3.2 MV. γ ray they yet pointed out that errors of measurement or unrecognized deflections of the tracks might have been responsible.

Alichanow, Alichanian and Kosodaew⁽³⁾ analysed the energies of the electrons liberated from lead, using semicircular magnetic focusing and counters. Their main curve could be accounted for by the known γ rays, but beyond the tail of the spectrum due to the 2.62-MV. γ ray they found a small hump in the region of 3.2 MV. The effect seemed to be very slight and only of the magnitude of possible probability-fluctuations.

Simons and Zuber⁽⁴⁾, although they are careful not to overstate their result, appear to have obtained indications that this γ ray is considerably more intense. They used a cloud chamber containing in turn argon and methyl iodide to investigate the production of positron-electron pairs, and they concluded that "if it be assumed that all the pairs of total energy greater than 2.0 MV. arise from this radiation, then it follows that there may be 0.12 ± 0.06 quanta of this higher energy per quantum of the lower energy (2.63 MV.)".

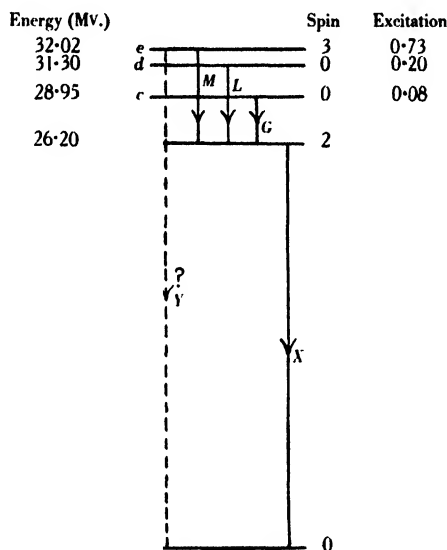
There seems little doubt that this 3.2-MV. γ ray has been detected, but the data as to its intensity are unsatisfactory. Since it is just this point that has such an important bearing on the applicability of the nuclear selection rules, it seemed worth while to attempt to obtain additional information. The results of the present experiment, while compatible with a weak intensity, render it improbable that the number of quanta of the 3.2-MV. γ ray is more than about 2 per cent of the 2.62-MV. γ ray.

§ 3. THE PRESENT EXPERIMENTS

The method of investigation chosen was to use the disintegration of the deuteron. It is well known that γ rays of energy greater than about 2.2 MV. lead to the disintegration of this nucleus, the proton and the neutron sharing approximately the excess energy. Thus the 2.62-MV. γ ray of ThC" gives recoil protons of about 0.2 MV. energy and these can be recorded by means of a suitable ionization chamber attached to a linear amplifier. The 3.2-MV. γ ray should give recoil protons of about 0.5 MV., that is kicks of more than twice the size. In addition, since in this region the probability of disintegration increases with the excess energy, the method should be more sensitive to the γ ray of higher frequency. Certain factors had to be considered in the design of the ionization chamber. In deuterium at atmospheric pressure the ranges of the two types of recoil protons would be about 1.4 and 3.8 cm., and unless the linear dimensions of the ionization chamber were large compared to these there would be a high probability of a proton hitting the side of the chamber before it had completed its full range. There are many disadvantages in using a very large chamber, so it was decided to fill the chamber with a mixture of 40 per cent of deuterium and 60 per cent of carbon dioxide, which has about the stopping power of air. In this mixture the ranges are approximately 3.3 and 8.6 mm. The collecting electrode was in the form of a plane grid of diameter 6 cm.

arranged midway between two plane electrodes also of 6 cm. diameter, and each electrode was at a distance of 3 cm. from the grid. This electrode system defining a cylinder 6 cm. in diameter and 6 cm. long was contained in an earthed brass box 12 cm. in diameter and 10 cm. long. With 4000 v. applied between both extreme electrodes and the grid there was an approximately uniform collecting field of 1300 v./cm.

A radiothorium source of 2.7 millicuries was placed at a distance of 16 cm. from the centre of the ionization chamber and surrounded with lead, the thickness of which in different experiments was varied between 1 and 3 cm. The number of ions corresponding to a given size of kick had been previously determined by using α particles of known range. The size of the proton kicks due to the 2.62-MV. γ ray



were found to correspond to an energy of 0.24 MV. with an uncertainty of about 20 per cent, and this is in rough agreement with previously known data. The number of such kicks observed in different experiments was consistent with the various degrees of filtering of the γ rays, and the total number agreed approximately with that calculated from the cross-section of the deuteron.

The overall amplification of the recording system was varied several times, but in each experiment a careful search was made for kicks of the size to be expected from a 3.2-MV. γ ray. Observations were made for a total time of 4 hours, during which 400 disintegrations due to the 2.62-MV. γ ray occurred, and the natural effect with the source removed was also measured for an equal period of 4 hours. In a region ± 10 per cent on either side of the size expected from the 3.2-MV. γ ray there were 29 kicks without the source and 33 with the source. Taking a wider range of ± 20 per cent there were 50 kicks without and 56 with the source. These figures are sufficient to make it very improbable that the 3.2-MV. γ ray has 5 per cent of the intensity of the 2.62-MV. γ ray, for in that case, when account is taken

of the greater probability of absorption and small correcting factors there should have been about 29 extra kicks. Considering this experiment and the other evidence as a whole we may conclude that it is most probable that between 1 and 3 quanta of the harder γ ray are emitted for every 100 quanta of the main 2.62-MV. γ ray.

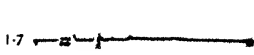
Reference to the figure will show that there is a γ ray M of energy 0.58 MV. which is due to a transition also starting from the uppermost level. Since its intensity, in quanta, is 0.7 of that of the 2.62-MV. γ ray, we can conclude that it is about fifty times more intense than the 3.2-MV. γ ray which is also associated with the same initial level. The probability of a transition will involve, among other factors, the frequency of the radiation emitted, in the sense of rendering more probable the emission of the higher frequency. That in spite of this the intensity of the permitted transition M is so much greater than that of the forbidden one Y is a strong proof of the practicability of the spin criteria.

§ 4. ACKNOWLEDGEMENT

It is a pleasure to acknowledge the able assistance I have had in these experiments from Mr R. D. Gander.

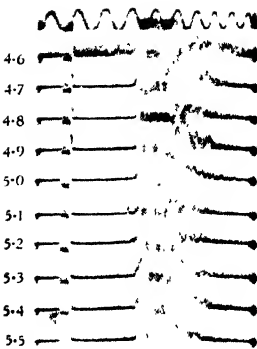
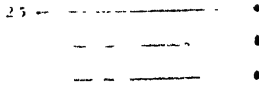
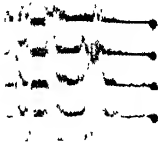
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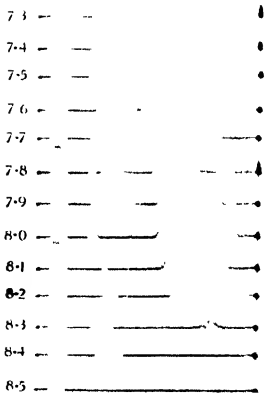
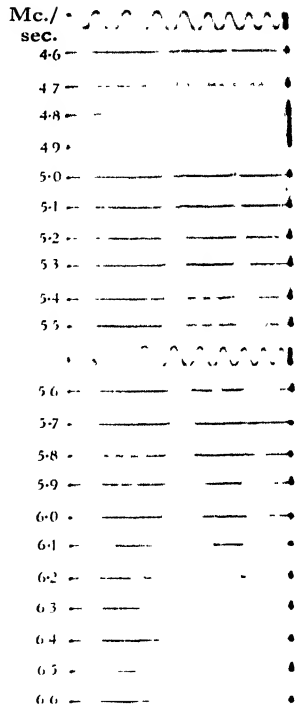


Mc./
sec.

No echoes observed 15-17 Mc/sec. incl.
1.8



7 February 1936.
(a)



10 April 1936. Start 1035.
Finish 1055.
(b)

10 April 1936.
(c)



1700

21/22 January 1936.

(d)

9/10 June 1936.

(e)

Plate 2.

HIGH-LATITUDE RADIO OBSERVATIONS

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AND

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ABSTRACT. Observations were made on the ionosphere for nearly a year at $80^{\circ} 23' \text{ N.}$, $19^{\circ} 31' \text{ E.}$ It was found that at local noon the E region was present throughout the winter except on a few days which were magnetically disturbed. The electron-density in this region is at a minimum at midwinter and a maximum at midsummer. The F_1 region is observed at noon only during the summer months with maximum electron-density at midsummer. The annual variation of maximum ionization in the F_2 region is irregular and not very great, but the electron-density is at a maximum in spring and in late autumn. The diurnal variation of electron-density in the F_2 region is more marked in the dark period, with a day to night ratio of $2.3:1$, than in the summer solstice period when the ratio is $1.5:1$. This latter figure which is also the ratio for the E and F_1 region is in fair agreement with the ratio of $1.63:1$ deduced theoretically on the assumption that the ionizing power is proportional to the altitude of the sun. In all cases the minimum is near midnight with maxima before and after noon and a subminimum near noon.

The effect of magnetic storms is to increase the electron-density in the absorbing region below the E region and, in the summer, to reduce markedly the electron-density in the F_2 region. Reflections from the persistent E region persist to very high frequencies especially between 1200 and 1800 G.m.t.

An intense E region, with a high reflection coefficient, occurs at all seasons during magnetically quiet conditions, and occurs almost solely between 1400 and 2300 G.m.t.

No special conditions in the ionosphere obtain when the aurora is overhead, and absorption is not usually markedly increased under such conditions.

§ 1. INTRODUCTION

THE Oxford University Arctic Expedition, 1935–1936, to North-East Land provided an opportunity for carrying out research on the ionosphere, the special interest of working in such a high latitude being that during the winter for 127 days at sea-level the sun is below the horizon, and therefore during this period each region in the upper atmosphere is cut off from the direct effect of ultraviolet light and uncharged corpuscular radiation, except for such radiation as has already passed through lower regions of the atmosphere. Further, North-East Land is to the north of the zone of maximum auroral frequency. The only ionospheric observations previously made north of this zone were those of de Bruine at Angmagssalik during the polar year 1932–1933.

The expedition was given generous support by the Royal Society, by Oxford

University, the Royal Geographical Society, and other Societies. With the help of Prof. E. V. Appleton and of officers of the Radio Research Station at Slough, and with the benefit of the results (then unpublished) of the British Expedition to Tromsø during the international polar year, the following programme was drawn up, with a view to collaborating with the Union Radio Scientifique Internationale, so that the best results might be obtained: (a) a $\{P', f\}$ * observation at local noon every day; (b) a $\{P', f\}$ observation at each hour of the international days fixed by the Union Radio Scientifique Internationale; (c) continuous $\{P', t\}$ † recording as often as possible (on 2.6 Mc./sec. during the summer, and on 1.0 Mc./sec. during the dark period); (d) a number of $\{P', f\}$ observations during strong magnetic storms; and (e) $\{P', f\}$ observations on the solar eclipse on 19 June 1936, in accordance with the programme arranged by a subcommission of the Union Radio Scientifique Internationale.

Owing to the difficulty of transporting sufficient petrol, the number of $\{P', t\}$ records was limited to two observations per fortnight—on the two days preceding each international day—and continuously for a week at each of the equinoxes. Unfortunately it was not possible to take a self-recording magnetograph, and although we converted the Benndorf self-registering electrometer into a magnetograph it was not very sensitive, and it worked for only part of the season. Instead of (d), therefore, observations were made during clear days when the aurora was visible directly overhead. Further, owing to the unexpectedly high critical frequencies obtained, we were forced to economize in oscillograph recording paper by making observations only every 2 hr., instead of every hour, during international days. Otherwise the programme was carried out as planned, from 30 August 1935 to 13 August 1936. The results of the observations on the solar eclipse have been published elsewhere⁽¹⁾.

§ 2. EQUIPMENT, ETC.

The base hut in which the research was carried out was established on a rocky promontory in Brandy Bay at $80^{\circ} 23' \text{ N.}, 19^{\circ} 31' \text{ E.}$

The Breit and Tuve pulse method was used. The power was supplied by a 1-kva., 230-v., 50-c./sec. alternator, driven by a 2-b.h.p. Petter engine, which was governed and provided with a heavy flywheel that reduced the cyclic variation to 1 in 250. A frequency-meter provided a check on the supply frequency. Interference-suppression devices were fitted to the ignition, and commutator and slip-ring devices to the alternator.

The transmitter, similar to that used by Ratcliffe and White⁽²⁾, was housed in a small hut about 80 yd. from the main base hut, and was in telephonic communication with it. Its power was 75 w.

The aerials were horizontal dipoles with twin wire feeds. The aerials proper, as opposed to the feeders, were cut to resonate at 3.0 Mc./sec., but the feeders

* $\{P', f\}$ refers to a curve plotted to show the relation between the equivalent path P' followed by the atmospheric waves, and the frequency f .

† $\{P', t\}$ refers to a curve plotted to show the relation between the equivalent path P' followed by the atmospheric waves, and the time t .

themselves were cut to suit the topography of the site. Thus, the feeders for the sending aerial were about 25 ft. long, and those for the receiving aerial were about 60 ft. long. No attempt was made at impedance-matching for any particular frequency, and there probably was not much frequency-discrimination in the combined system. The aerials were each supported on three 30-ft. masts, and the central dip in each span was about 5 ft. The effective height was very low. The ground underneath consisted of boulders and sheets of rock. At a distance of less than a quarter of a mile there was a 1000-ft. cliff, rising to a mountain 1500 ft. high.

The receiver was in the main base hut. It was almost the same as that used at the Radio Research Station at Slough⁽³⁾.

For a $\{P', f\}$ observation the frequency of the transmitter was increased in steps of 0.1 Mc./sec. from 0.8 Mc./sec. up to the frequency on which echoes were no longer received. Coil-changes were made four times, so that it took about 20 min. to complete a record, and frequently on occasions of high critical frequency (necessitating changing the recording paper in the camera) it might take half an hour to complete the record. This was a considerable disadvantage, as frequently the conditions were changing with great rapidity. The length of the time base corresponded to an equivalent height of 700 to 1000 km. The camera was in the dark room, the lens and shutter being fixed in the wall which separated the two rooms. The drum was controlled from the living room, and for the $\{P', t\}$ records was driven by a clock, so that the paper-speed was about 4 cm. per hour.

The angle of dip of the earth's field was 82.5° , and the total field 0.53 ± 0.02 gauss, corresponding to a gyrofrequency of 1.49 Mc./sec.

The only difficulties encountered were with the insulation during the summer thaw and with the thyatron, which frequently did not strike within half an hour of switching-on, when the temperature was below zero Fahrenheit. We used, therefore, always to keep a warm-jacketed thyatron in the base hut, and on being substituted for the cold one it would strike at once.

§ 3. RESULTS

General results. It might be expected that at a latitude where the sun is below the horizon for $4\frac{1}{2}$ months during the winter and above it for $4\frac{1}{2}$ months during the summer the conditions in the ionosphere might be very different from those obtaining in lower latitudes. In general, however, the same ionized regions are observed in North-East Land as elsewhere. The *E* region which is observed almost always at noon is of three types: (1) The normal *E*, returning an undistorted echo which shows group retardation near the critical frequency, and does not reflect energy emitted at higher frequencies; (2) intense *E*, with a very high reflection coefficient, giving echoes up to the seventh order or more; and (3) persistent *E*, with a small reflection coefficient giving a sharp echo which shows no group retardation at its critical frequency, but is partially reflecting to pulses of a higher frequency.

An F region is always present: F_1 is absent in the winter, and F_2 absent only during very disturbed conditions in the summer, when F_1 is present. Very occasionally a distinct G region is visible above F_2 .

Reflections from the low D region, observed by Mitra and Syam⁽⁴⁾, were not observed. On 19 March 1936, at local noon, an echo was observed at an equivalent height of 55 km. on 2.8 Mc./sec. This is the only occasion on which an echo was observed below 85 km., and echoes below 95 km. were rare. In addition, echoes of an irregular type are liable to be seen in great numbers at random heights at any time and on any frequency.

It is not easy to define exactly these three different types of E region, but on examining the $\{P', f\}$ or $\{P', t\}$ records there is never any doubt as to which class an echo belongs. The normal E region has a reflection coefficient of the order of 0.1 to 0.2, the echoes show slight group retardation near the critical frequency and are not visible on higher frequencies: intense E region has a reflection coefficient of the order of 0.7 to 0.8 and usually persists as a partial reflector on frequencies above the critical frequency with a reflection coefficient which decreases as the frequency increases. Persistent E region has a reflection coefficient of the order of 0.1 or 0.2 below its critical frequency, but above it it has so small a reflection coefficient that though the first echo is at the saturation level there is no trace of a second echo; in other words, the reflection coefficient is not greater than 0.01.

It must be emphasized that the difficulties encountered in analysing the records are very great, especially in winter, and it is necessary to state here the criteria used in determining the critical frequencies. It often happens that after a few observations, 0.1 Mc./sec. apart, of a sharp single E echo, an echo is obtained which has apparently been reflected from a region higher than E , yet is not a definite F echo. This frequency is denoted by f^*E° . There may then be some pictures with only a single E echo, and some with echoes from greater equivalent heights, and a frequency is eventually reached on which an F echo is observed and continues on all higher frequencies. This has been taken as fE° . In the summer on the critical frequency thus determined by the appearance of F (rather than by the appearance of an echo above E), the E echo shows group retardation. It is thus the lowest frequency which will penetrate all ionized regions below the F regions. In the winter the E echo (of the α - E type) does not show group retardation and persists beyond this frequency as a partial reflection.

The determination of fF_1° presents no real difficulty. It is the frequency on which the $\{h', f\}$ curve shows group retardation, or bends over horizontally as echoes are received from a uniform height from the F_2 region.

In winter the echoes received from the F_2 region are very scattered and stratified: the lower edge of the echo on the oscillograph is sharply defined and its equivalent height varies regularly with frequency, but energy is received for a considerable time afterwards so that the total width of the reflected pulse is equivalent to 100 km. or more. (a) in plate 1 is a reproduction of part of the local noon $\{P', f\}$ record of 7 February 1936, and it illustrates the diffuse nature of the echoes received during the dark period. It illustrates too a phenomenon which is sometimes

observed, the gradual increase of the width of the echo with frequency and a sudden decrease in the energy received on a certain frequency, in this case 4.2 Mc./sec., suggesting the presence of a region for which this is the critical frequency, and yet the lower edge of the echo is continuous from one frequency step to the next.* Sometimes there is no doubt as to the value of fF_2° owing to group retardation, but usually the echoes continue to weaken and increase slightly in equivalent heights as the frequency increases, and disappear without any group retardation or sudden energy-loss for either the ordinary or the extraordinary ray. In the absence of any sure indication of a critical frequency we have been forced to take the highest frequency on which sensible echoes are obtained as fF_2^\times , and to take fF_2° as 0.8 Mc./sec. less than fF_2^\times . The critical values thus determined are of the same order as those determined at the same time of year when there is no doubt as to the critical frequency. It may be remarked, therefore, that whereas in the summer the pronounced group retardation ensures that the value of fF_2° shall be quite independent of the power of the transmitter, one would hesitate to say that the same is strictly true on many winter days.

On several days when the ordinary and extraordinary rays show group retardation, echoes continue regularly beyond fF_2^\times at an equivalent height slightly greater than F_2 . This has been taken to be a spur on F_2 , but it must be mentioned that this spur reflects only the extraordinary ray, never the ordinary. Very occasionally the height-separation is greater, and the upper region is more in the nature of an F_3 region than a spur on F_2 .

The contrast between the scattered winter echoes as at (a) in plate 1 and the sharp clean echoes in the summer as at (b) in plate 1 is very striking. The cleaning up begins to be noticeable at noon a few days after the first sunrise.

On most occasions some echoes were received from the region between the E region and the F region. These echoes are only very rarely regular enough to be said to be reflected from an E_2 region, and we refer to all echoes received from this intermediate region as J echoes. Sometimes echoes were received from all heights above the E region, so that on the oscillograph pattern the E , J , and F echoes are all joined. J echoes are most commonly seen on frequencies above and within 1.0 Mc./sec. of fE° . They almost always occur as partial reflections, rarely as from a totally reflecting layer.

Rather of the same nature, but distinct from them in their occurrence, are what we call the *polar echoes*. These are first seen on a high frequency and continue irregularly sometimes to a frequency greater than fF_2^\times and sometimes so strongly as to obscure the F region. These echoes are shown at (c) in plate 1 below the F echoes, beginning at about 6.5 Mc./sec. and continuing to 8.4 Mc./sec. Sometimes the equivalent height h' of one of these echoes varied rapidly with time so that the echo could be seen moving about on the oscillograph screen. As a rule, however, h' was constant for a given frequency, but the amplitude of the echo changed rapidly and h' varied erratically from one frequency to the next. The polar

* In the reproduction, the frequency of the calibrator was 1500 c./sec., so that the distance between each wave is equivalent to 100 km. equivalent height.

echoes occur at any equivalent height between 100 and 250 km., and sometimes at greater equivalent heights, and are distinct from the ordinary J echoes in that no echoes are obtained from these heights over the frequency range lying between fE° and about 5.5 Mc./sec., the frequency at which the polar echoes generally first appear.

Local noon observations. The monthly means of the heights and critical frequencies for the E , F_1 and F_2 layers are plotted in figure 1, with the locus of the earth's shadow at local noon, and those for the critical frequencies are plotted in figure 2 with the monthly means at Tromsø for the same period, kindly sent to us by Dr Harang.

No distinction has been made between ordinary E and persistent E : in the winter the E region is always of the persistent E type, and in the summer is nearly always the normal E . On a few occasions both types are present at the same time. During the intermediate period when the E region is sometimes of one and sometimes of the other type, there is no tendency for one type to be either higher or more densely ionized than the other.

Figure 1 shows that the equivalent height of the E region is greater in winter than in summer, averaging 123 km. in December and 102 km. in June. This is to be expected on the assumption that the ionization is due to rectilinear radiation from the sun. Both the equivalent heights and the critical frequencies are more variable from day to day in the winter than in the summer. There is no discontinuity in the critical values at the time when the earth's shadow reaches the E layer at noon, or at any other time. The critical frequency follows an inverse curve with a maximum at midsummer and a minimum at midwinter. The f^*E° curve is rather similar, but more irregular, and with the maximum and minimum occurring earlier.

The Tromsø curve for fE° is not continuous throughout the winter, for an E echo was never obtained there during undisturbed conditions when the sun was below the horizon. It should be noted that a similar result was obtained at Tromsø during the polar year three years previously, and near a sunspot minimum.

The F_1 region was observed on three isolated occasions during September but was not observed during the winter until 21 March. It was present at noon on 7 days at the end of March, was absent from 1 to 7 April and was nearly always present after 8 April. It is very interesting to note that the F_1 region was not observed at Tromsø until 2 May: it is difficult to understand why it should be formed 6 weeks earlier than this at a station some 700 miles further north. It is true that the days are then longer at North-East Land than at Tromsø: nevertheless the ionizing factor which is proportional to $\int \sin h \, dt$ integrated from sunrise to noon, is greater at Tromsø. fF_1° is a maximum at midsummer and, as in the case of fE° , the critical values in the main follow a $\sin^{\frac{1}{2}}h$ curve, where h is the sun's altitude at noon.*

The fluctuations from day to day of fF_2° are very large, especially during the winter. The monthly means do not give a smooth curve, but it is clear that there are

* See p. 226.

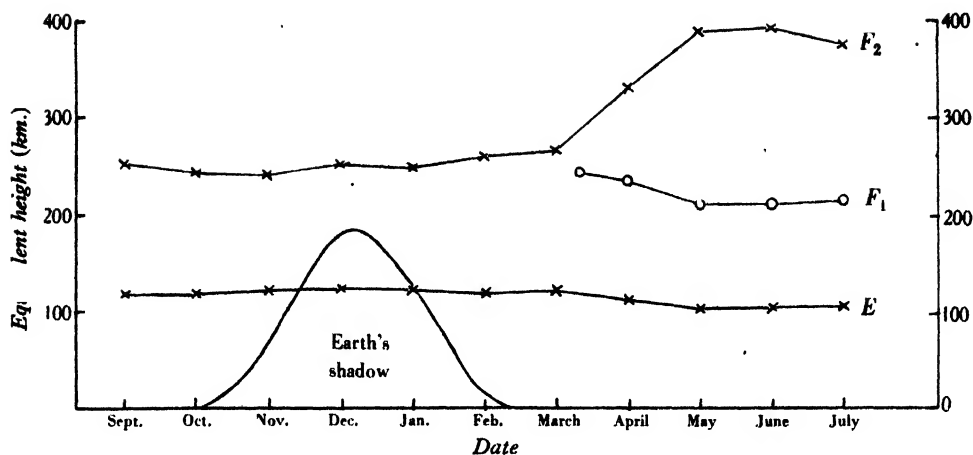


Figure 1.

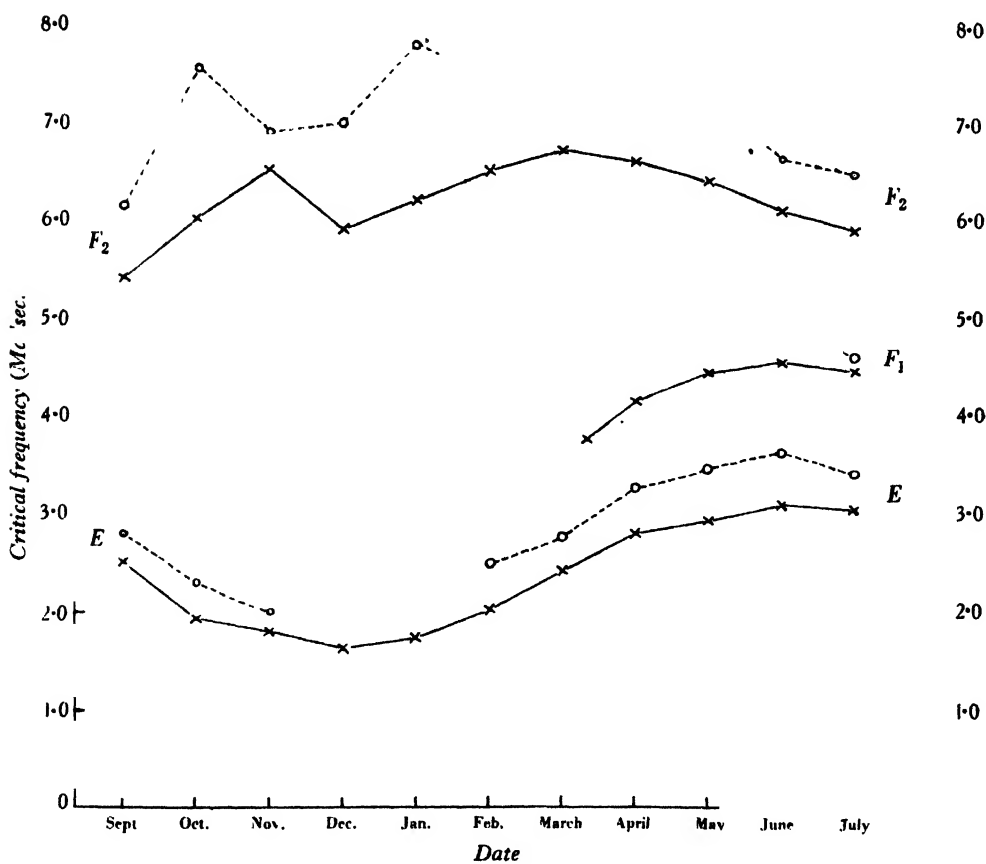


Figure 2. ○-----○ Tromsø; ×——× North-East Land.

ionization maxima in November and in the spring. It should be noted that the autumn maximum occurs earlier at Tromsø than at North-East Land. It should be recorded that even if we regard the spur as a part of F_2 , and take always as fF^\times the frequency required completely to penetrate F and the spur and anything above it, and if we take fF° as given by fF^\times less 0.8 Mc./sec., then averaged over a month these values of fF° differ from those of fF_2° in the table by only 0.1 to 0.3 Mc./sec., and the general shape of the curve of monthly means is unchanged.

During the winter when no F_1 region is present, the daily fluctuations of $h'F_2$ are not large, rarely differing from the mean by more than 30 km., but during the summer when F_1 is present the F_2 layer appears to be pushed upwards and its equivalent height fluctuates from 200 to 600 km.

A phenomenon which is difficult to understand was observed on twelve occasions during the summer: the ordinary and extraordinary F_1 echoes are clearly visible with a separation agreeing well with the theoretical value of 0.76 Mc./sec., but besides them a weak but very clear echo can be distinguished and traced on all frequencies, behaving exactly as the ordinary component but with a critical value smaller by only from 0.4 to 0.5 Mc./sec.

The correlation coefficient between the local noon values of fF_2° at Tromsø and North-East Land is very small and is greater in summer than in winter. Its value is +0.19 from November to February inclusive and +0.29 from April to July inclusive.

Diurnal variations. The change of conditions during the day can be studied from the records of 22 international days, on which $\{P', f\}$ observations were made every 2 hr. from 1600 h. G.m.t. to 1600 h. on the next day, and from seventy $\{P', t\}$ records on 2.0 Mc./sec. during the winter and on 3.0 Mc./sec. during the summer, with a period of a week at the equinoxes when observations were made on alternate frequencies on alternate days.

It is most convenient to study the diurnal variations during three different periods: (a) from 19 October to 25 February, the dark period, when the sun is permanently below the horizontal, so that any diurnal variations of ionization must be due either to non-rectilinear rays from the sun or to rectilinear rays which have already passed through a considerable thickness of atmosphere or to the transport of ions from lower latitudes; (b) from 15 April to 29 August, the sunshine period, when the sun is permanently above the horizontal; and (c) in the summer-solstice period when the sun's declination is greater than 18° N.

The heights and critical frequencies at each even hour of the day are averaged for the 8 international days during the dark period and for the 6 international days during the summer-solstice period, and are shown in figures 3 and 4. A comparison of the means of the records taken at 1600 h. at the beginning of the 24-hr. period with those taken at 1600 h. at the end of the period gives some idea of the general accuracy of these average values.

During the dark period the diurnal variation of only the F_2 region can be considered because, though E echoes are very frequently received, the critical frequency of the E region is, except near noon, usually below the absorption level, so that it

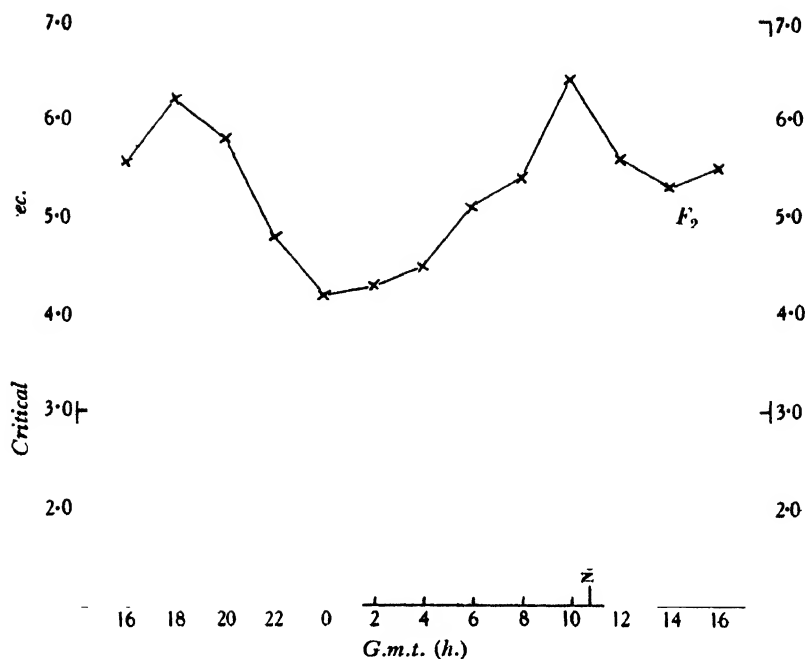


Figure 3. Dark period.

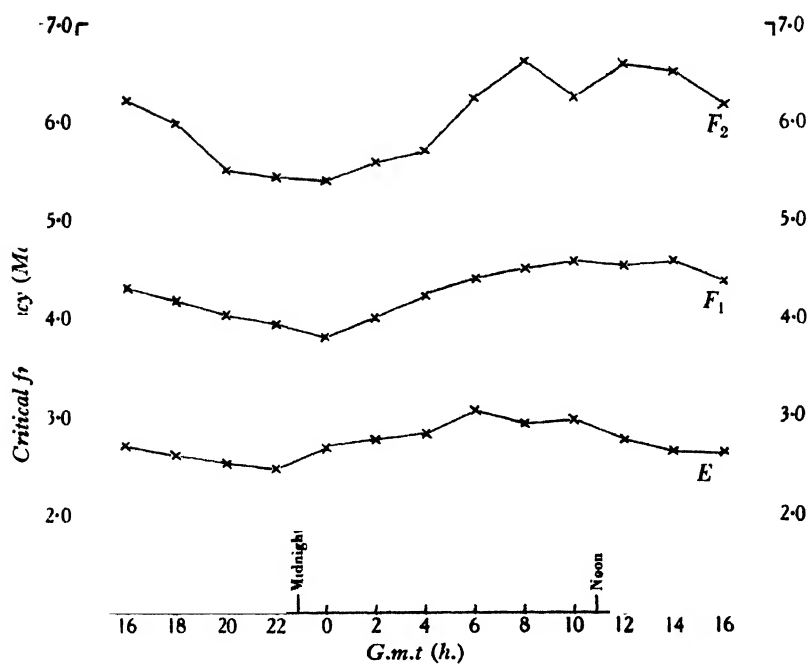


Figure 4. Summer solstice period.

has already been penetrated when echoes are first received. Sometimes the critical frequency can be determined but, except near noon, there are not enough determinations for an average to be taken.

The ionization in the F region is a minimum soon after midnight, rising to a maximum just before local noon: there is an afternoon minimum rising to an evening concentration at about 1800 h. These results are not merely the effect of averaging and including one or two abnormally large values, for of the eight records from which the averages are taken, six show an evening maximum at 1800 or 2000 h. and five show a minimum at 1200 or 1400 h. On every occasion the curve of diurnal variation was approximately of the shape of the curve of averages, with high readings during the hours near noon and low ones near midnight. The electron-densities corresponding to the noon maximum and the midnight minimum are 7.6×10^5 and 3.3×10^5 electrons per cm^3 , the day-to-night ratio being thus 2.3:1.

During the summer-solstice period the ionization is a minimum near midnight in the E , F_1 and F_2 regions, and broadly speaking a maximum near noon. There is one very low point on the curve for region F_2 at local noon, and the maximum on the curve for region E precedes local noon slightly, although the curve is very flat about that time.

Table 1

Layer	N (10^5 electrons per cm^3)		Ratio of maximum to minimum
	Max.	Min.	
E	1 68	1 12	1 50
F_1	3.96	2 70	1 47
F_2	8 15	5 45	1 50

If rectilinear radiation from the sun were the only ionizing agent we should have at the maximum and minimum

$$\frac{dN}{dt} = Q \sin h - \alpha N^2 = 0,$$

where h is the sun's altitude, Q the ionizing power when the sun is overhead, and α the recombination coefficient. So if α be assumed to be constant

$$\frac{N_{\max}}{N_{\min}} = \sqrt{\frac{\sin h_{\max}}{\sin h_{\min}}}.$$

The maximum and minimum are respectively very near noon and midnight, and taking the average declination of the sun over this period as $20\frac{1}{2}^\circ$, we have

$$\begin{aligned} \frac{N_{\max}}{N_{\min}} &\approx \sqrt{\frac{\sin 30^\circ}{\sin 11^\circ}} \\ &\approx 1.63. \end{aligned}$$

This theoretical value is greater than the value actually obtained. This is what we should expect, however, for the heating and rarefaction of the atmosphere during

the day and the cooling and contraction during the night would tend to reduce the day-to-night ratio of electron-density. It will be seen that the electron-density at midday during the dark period, when the sun is below the horizontal (as much as 14° below the horizontal at midwinter), is greater than at midnight during the summer solstice.

In contrast with these results it must be pointed out that at Tromsø during the polar year the region F_2 critical frequency was actually greater at midnight than at midday during the period of the midnight sun⁽⁵⁾.

Magnetic disturbances. To determine the time of day at which magnetic disturbances occurred most frequently, the magnetograms were examined and the

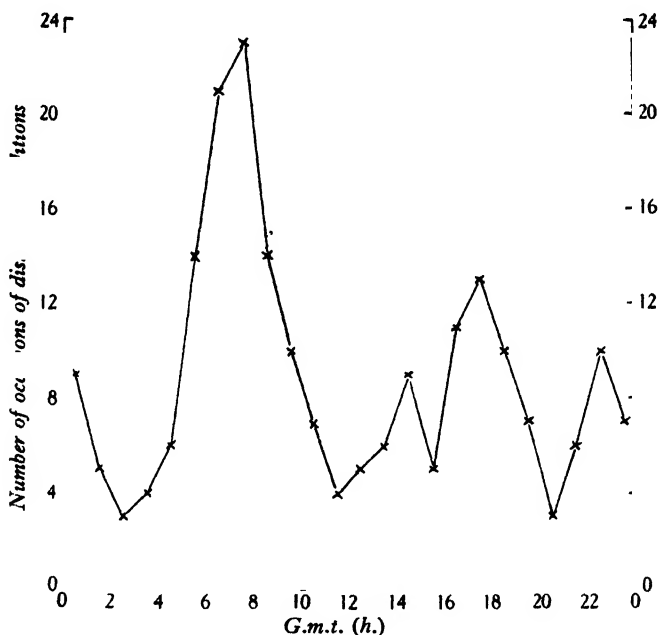


Figure 5. Times of occurrences of magnetic disturbances.

number of times when a magnetic storm occurred during each period of 1 hr. between two successive hours was counted. As was mentioned above, the magnetograph was by no means sensitive and the criterion of a storm is merely qualitative, but the resulting curve, figure 5, leaves little doubt that the most disturbed period is between 0500 and 0900 G.m.t., while there is a minimum near local noon and a small maximum between 1600 and 1900 G.m.t. This is the result of analysing the records of the whole year, but during the autumn and winter it was the latter period that was the most disturbed, and only after January did the early morning period become much more disturbed than any other time of the day. The number of days from which the analysis has been made is 122. The magnetic conditions at local noon were described qualitatively and compared with Dr L. Harang's qualitative description of the conditions at Tromsø. The agreement is quite good: the condition of quiet at one station usually corresponds to quiet or small disturbance

at the other, and so on, and on only 4 days out of the 121 on which comparisons have been made were the magnetic conditions very different. We feel reasonably justified, therefore, in referring to the magnetic conditions at Tromsø on days when we have no magnetic record available.

Direct comparison between ionosphere conditions and magnetic data. On no occasion was it found impossible to obtain any reflections at all, as reported elsewhere, though on 2 April 1936 at local noon only a few echoes were obtained near 7.0 Mc./sec. $\{P', f\}$ observations were made every 2 hr. after local noon on this day to examine the rate at which conditions returned to normal. The absorption limit—that is, the frequency on which echoes are first observed—fell slowly, and by 1900 G.m.t., $8\frac{1}{2}$ hr. after local noon, the first echo from the E region was received on 2.5 Mc./sec. It remained for the next 6 hr. until observations ceased, though even this is above the average absorption-limit frequency at this period of day and year. The critical frequencies were a trifle high but not at all abnormal, and the layer-heights were normal, so we conclude that the storm affected only the region below the E region.

The $\{P', t\}$ records sometimes show a sudden cessation of all echoes—probably a sudden commencement of absorption as there is no group retardation and the frequency is much lower than any critical frequency ever recorded. On every occasion for which magnetic records are available the sudden absorption was accompanied by a sudden magnetic disturbance. If we consider only periods of less than 1 hr. during which no echoes were received, it can be stated that when persistent E and F echoes have been previously obtained, then the echo pattern is unchanged when echoes appear again, but if F echoes only have been observed before cessation, then either F echoes appear alone afterwards, or else a weak E region appears first and masks the F region for perhaps half an hour, when it becomes partially reflecting and the F region is visible again. (d) in plate 2, a $\{P', t\}$ record on 2.0 Mc./sec. on 21/22 January 1936, shows a sudden cessation at midnight and the corresponding magnetogram shows a sudden disturbance at the same time.

On twenty-one occasions at local noon—and these were all between September and February inclusive—the critical frequency of the E region could not be determined, as the F region was visible on the lowest frequency on which echoes were observed. On only one of these was the absorption frequency above the average, so that on twenty occasions the ionization of the E region was unusually small. On these occasions as a rule the magnetic conditions were disturbed, usually stormy, and at 10 h. (M.E.T.) at Tromsø on these days there is usually a no-echo condition. Further, on these days, the critical frequency of F_2 region at North-East Land is almost always considerably below the average.

Direct examination of the equivalent heights and critical frequencies on days classified as quiet and stormy respectively shows that there is no tendency at any season for $h'E$, fE° , $h'F_1$, or $h'F_2$ (in winter) to adopt, on either class of day, values above or below the general average, but that fF_2° is almost always above the average on quiet days and is always below the average on stormy days. fF_1° shows a small but definite tendency in the same direction.

The effect of a very big storm during the summer is to cause $h'F_2$ to become very large and fF_2° to become low, so much so that at times the F_2 echoes cannot be seen, indicating either that the layer is so high that the echoes are beyond the end of the time base, or else that the critical frequency has fallen below that of the F_1 region. Frequently too the echoes are very weak, with the E echoes appearing first normally at about the usual frequency (about 1.6 Mc./sec.) but with a no-echo condition on frequencies from about 3.3 to 4.5 Mc./sec.

The fact that maximum ionization is reduced during magnetic storms is important, for it is contrary to expectation. It means that ions, instead of being produced, are either lost during a discharge or are redistributed throughout a greater volume because of the lowering of density accompanying the thermal expansion of the atmosphere.

Persistent E. One of the most striking features of this phenomenon is the manner in which strong undistorted partial reflections persist to a high frequency. The highest frequency on which echoes are detected from the persistent E region is referred to in this communication as the *persistence frequency*. Persistent E occurs only during magnetically quiet periods.

There is no marked seasonal variation, but the diurnal variation is very marked. If we adopt, and extend, the convention used by the British Polar Year Expedition at Tromsø and give a weight 1 to all occasions when the persistence frequency is between 2.6 and 5.2 Mc./sec., a weight 2 when the persistence frequency is between 5.2 and 7.8 and a weight 3 for higher persistence frequencies and add the results for every even hour of the day, we obtain the values shown in table 2.

Table 2

G.m.t.	Total	G.m.t.	Total	G.m.t.	Total
1600	21	0200	5	1000	4
1800	20	0400	3	1200	14
2000	12	0600	5	1400	18
2200	6	0800	4	1600 ^a	22
0000	7				

The figures are derived from the 286 international-day records, with twenty-two records at each of the hours. Persistence frequencies greater than 8.0 Mc./sec. were observed on fourteen occasions, all between 1200 and 1800 h. inclusive.

Aurora. Owing to shortage of personnel and the almost persistent cloudiness, insufficient observations were made between 0000 and 0700 h. to determine the time of maximum frequency of the aurora. The auroral arcs and bands were predominately in the south, but sometimes a weak corona was visible overhead, and occasionally bands from the south passed overhead and set in the north. A number of $\{P', f\}$ observations were made when aurora was visible overhead or soon afterwards. There is no feature common to all the records, and evidently the effects of aurorae can be very different. On some occasions the absorption frequency is higher than normal, but on no occasion did the no-echo condition obtain. The only generalizations that can be made are (1) that the F region seems always to be quite normal, and (2) that conditions change very rapidly in the course of a few

minutes, so that one record would be very different from another taken 10 min. later.

Results of the $\{P', t\}$ records. The diurnal variation of the electron-densities cannot be directly studied from the $\{P', t\}$ records, but the probability of pene-

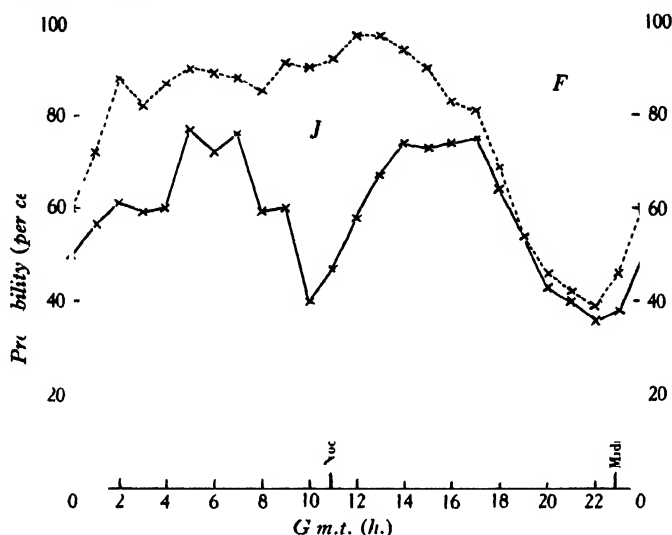


Figure 6. Dark period, 20 Mc/sec

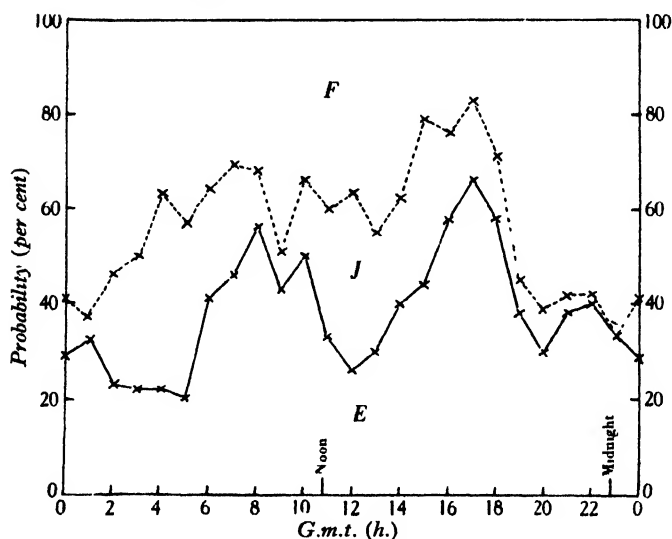


Figure 7. Sunshine period, 30 Mc/sec.

trating certain regions with 2.0 Mc./sec. in the winter and with 3.0 Mc./sec. during the summer can be calculated. Figures 6 and 7 represent the results of the 2.0-Mc./sec. $\{P', t\}$ records during the dark period, and of the 3.0-Mc./sec. records during the sunshine period. The lower curve represents the percentage probability that the lowest echo is reflected from the *E* region, i.e. that h' is less than 130 km.,

and the dotted line is the probability of the lowest echo being reflected from either the *E* or the *J* region, i.e. of h' being less than 180 km., so that the distance between the curves is the probability that the lowest echo is a *J* echo, and the distance above the dotted curve is the probability that the lowest echo is an *F* echo. The curves are not dissimilar to the curves showing the diurnal variations of the critical frequency, with a night minimum and a daytime maximum with a subminimum near midday. It can be seen too that the *J* echoes are very rare near midnight, a fact which suggests that the diurnal variation of ionization in this intermediate region is greater than that in the *E* region.

Intense E. Table 3 shows the number of times intense *E* was observed on the $\{P', t\}$ records at each hour of the day. The total number of observations at each

Table 3

G.m.t.	Number of occurrences	G.m.t.	Number of occurrences	G.m.t.	Number of occurrences
1	2	9	1	17	11
2	1	10	0	18	8
3	0	11	—	19	9
4	0	12	1	20	6
5	0	13	1	21	8
6	0	14	4	22	6
7	1	15	3	23	2
8	0	16	13	0	1

hour is about 70, so that intense *E* occurs on nearly 20 per cent of the occasions at 1600 h. The evening maximum is very pronounced, and intense *E* is rarely observed from 0000 to 1200 h. In eleven months it was observed only once at local noon. It seems to be more common near the equinoxes than near the solstices, but the number of observations is not really great enough for this to be stated definitely. Intense *E* does not begin very suddenly, but the reflection coefficient seems to grow quickly and then to decrease slowly as in the reproduction of the 3.0 Mc./sec. $\{P', t\}$ record of 9/10 June 1936 at (e) in plate 2. Intense *E* occurs only in magnetically quiet conditions.

Irregular echoes. The polar echoes were observed strongly on 30 of the 294 local-noon records, and weakly on many more. Irregular echoes similar to the polar echoes but visible on all frequencies occurred on 35 local-noon observations. Neither type tends to occur at any special time of day, and both are most common during October, November, December and January, though they occur also in the summer. These echoes occur in all conditions of magnetic activity.

It seems that during these times the maximum ionization in the intermediate region between *E* and *F* is very little less than in the *E* layer, and that these random echoes are returned from ion-clouds or ion-concentrations where the ionization is greater than the normal. Since these echoes occur in the winter as well as in the summer, it seems that the clouds must be formed perhaps by local ionization caused by a burst of charged particles from the sun, or possibly from ion-clouds formed by meteors as suggested by Skellet and observed by several observers⁽⁶⁾. If the former is the real cause it is surprising that there is no correlation between the occurrence

of polar echoes and the magnetic conditions: if the latter it is not easy to see why the echoes should be observed to such an extent in high latitudes.

In the past many echoes have been observed for which a satisfactory explanation is difficult to find, so we do not hesitate here to record that on twenty-three occasions we obtained photographs—54 photographs in all—of echoes with equivalent heights between 500 and 640 km. on frequencies between 1.4 and 2.3 Mc./sec., and once on frequencies between 2.8 and 3.4 Mc./sec. Sometimes an *E* echo is visible at the same time and sometimes not. No special magnetic conditions are favourable to the reception of these echoes. We believe them to be genuine echoes for (1) they have the appearance of echoes, definite and sharp with a break in the time base line, showing that they are in synchronism with the pulse for the 20 cycles of the a.-c. supply during the exposure of $\frac{2}{3}$ sec.; (2) we were very far from any disturbing source other than in our own a.-c. supply; and (3) the slightness of the variation of equivalent height makes it unlikely that they are caused by a spot on the commutator or some other local periodic disturbance.

At times conditions are changing very rapidly, so that the echo pattern has changed very noticeably during the period of about 2 min. during the change of an inductance at the receiver. Only one of the days on which this was marked was stormy: usually magnetic conditions were quiet or slightly disturbed.

Many great-circle communication routes between important centres pass through Arctic regions, and if direct wireless communication between these places is to be reliable, it will be necessary to understand the various changes taking place in this part of the ionosphere and to predict the times and frequencies at which conditions will be best for communication. During the winter, conditions in the ionosphere are very erratic though the absorption is low. Communication is difficult at all seasons during periods of strong magnetic activity.

§ 4. ACKNOWLEDGEMENTS

We wish to express our sincere thanks for the invaluable help and advice given to us by Prof. E. V. Appleton, by Mr R. Naismith and other officers of the Radio Research Station at Slough, and by Dr Leiv Harang of the auroral observatory, Tromsø, who has kindly provided us with relevant data from Tromsø and given us permission to refer to them. We wish also to thank the Department of Scientific and Industrial Research for the loan of the receiver; Prof. Townsend, in whose laboratory most of the apparatus was made; the many British firms which supplied us with apparatus either free or at reduced prices; and the Royal Society and other learned bodies, without whose moral and financial help the expedition could not have taken place.

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THE DIURNAL VARIATION OF THE IONOSPHERIC ABSORPTION OF WIRELESS WAVES

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ABSTRACT. Experimental determinations of the reflection coefficient of wireless waves reflected from the *F* region of the ionosphere are described. The afternoon variation of the reflection coefficient was investigated on several days between June and December 1936. Days with a quiet ionospheric behaviour were chosen, and the tests made in choosing such days are described. The results can be explained on the assumption that the absorption occurs in the lower portion of a simple *E* region of the type considered by Chapman. It is shown that the recombination coefficient must be independent of the pressure at heights above 110 km. at least, and that it must have a value not less than 10^{-8} . It is pointed out that this value does not fit in with the usually accepted theory. The absorption measurements are shown to be in agreement with Martyn's⁽¹⁾ suggestion that the collisional frequency for electrons in the neighbourhood of the *E* region is given by assuming that the value at a height of 90 ± 5 km. is 10^6 per second and that the scale-height of the atmosphere is 9 km.

§ 1. INTRODUCTION

THIS paper is concerned with the absorption of waves reflected from the *F* region of the ionosphere at vertical incidence. It has previously been shown⁽¹⁾ that, except under conditions of marked group retardation in region *F*, the absorption of these waves is determined by their passage through the *E* region, and in this paper we attempt to make deductions about the structure of the *E* region from observations on the amplitude of the *F*-region echoes. The observations recorded were made on occasions when the *E*-region behaviour was quiet, and our criteria for quiet conditions are described in § 2. The object of the experiment was to investigate the variation of the *E*-region absorption (of *F*-region echoes) with the sun's zenith angle throughout the afternoon, and to see how far the behaviour on quiet days could be explained on the simplest possible picture of the *E* region.

The experiments and experimental results are described in § 2. In § 3 a theoretical investigation is made of the way in which the absorption of *F*-region echoes would vary with the sun's zenith angle on the simplest possible assumption that all the absorption occurs in an *E* region of the type suggested by Chapman⁽²⁾. In § 4 the conclusions are compared with the experimental results, and in § 5 it is suggested that deductions can be made about the processes of electron-loss in the *E* region.

The experiments are in some ways similar to those described by Prof. Appleton in his Bakerian Lecture⁽³⁾ to the Royal Society, in which the seasonal variation of

midday absorption was studied. Appleton discusses this seasonal variation of absorption in terms of the sun's zenith angle and comes to conclusions similar to those outlined here, with one exception mentioned in § 4.

§2. EXPERIMENTAL ARRANGEMENTS AND RESULTS

The observations were made at Cambridge, during the second half of 1936, with a Breit and Tuve pulse transmitter and a receiver about 1 mile apart. The transmitter frequency could be varied by a remote control from the receiver. A cathode-ray oscillograph was used in conjunction with a time sweep, in the usual way, and was observed visually.

For the absorption-measurements a fixed frequency was used on any one day, and was selected as follows. Before a day's experiments were started the curve

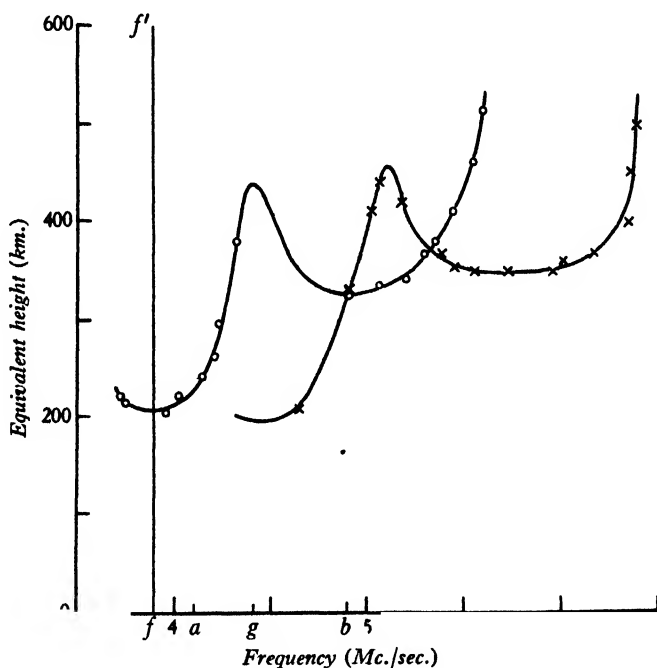


Figure 1. $\{P', f\}$ curve for the F region in summer.

relating equivalent path P' to frequency f was examined, and a frequency was selected which gave reflections from the F region with no magneto-ionic splitting due to region F_1 . A typical $\{P', f\}$ curve is shown in figure 1 and the frequency selected corresponded to the point marked f . During the afternoon the F region alters so that the $\{P', f\}$ curve drifts to the left, and the fixed frequency corresponds in turn to points more and more to the right of the line $f-f'$. Near the point g there occurs considerable splitting of the echo, and retardation of one component due to the F_1 region. The absorption produced by this retardation will be discussed later. Since the frequency on which observations were made was chosen afresh each

day it was not the same at different times of the year: it varied from 4.2 Mc./sec. in June to 3.2 Mc./sec. in December. Measurements of intensity were made by noting the reading of a calibrated gain-control required to bring the echo-amplitude to a given mark on the oscillograph screen. This sufficed for the measurement of relative amplitude, so that the variation of reflection coefficient with time of day could be determined. From time to time the amplitude of the ground wave was measured in the same way to make sure that the transmitter had not changed. Towards sunset, when the amplitude was greater, it was possible to obtain absolute values for the reflection coefficient by comparing the first and second reflections, and then the values obtained earlier in the day could be converted into absolute values also.

The amplitude measurements were made by averaging through intervals of 5 min. In order to determine the extent to which two such averages are significantly different, two sets of amplitude observations, separated by about half an hour, were taken in the afternoon, when the echo-amplitude was increasing. In each set amplitudes were observed every 5 sec. for a period of 10 min. The means were 2.28 and 3.33 respectively and the standard deviations 0.12 and 0.175; it follows that the standard deviation for the difference of the means was 0.21. The condition for a significant difference between the two means is that it should be greater than twice its standard deviation and this is clearly satisfied by the data. It may be deduced that two means separated by 10 per cent are just significantly different. In the routine amplitude measurements the averages were not obtained with the same precision, but differences of 50 per cent or more may be taken as real differences of the same order.

At intervals of 30 min. an observation was made of the penetration of the *E* region; this observation took usually about 10 min. In the earlier of our observations the two threshold frequencies at which (a) *F*-region echoes first appeared, and (b) *E*-region echoes disappeared, both with increasing frequency, were observed, and a day's observations were not used unless both these frequencies behaved smoothly and regularly throughout the day. We have given reasons elsewhere⁽²⁾ for supposing that these conditions represent what may be considered as quiet ionospheric behaviour. Later in the year conditions were made even more stringent and a detailed $\{P', f\}$ curve was taken in the neighbourhood of the *E* penetration frequency every 30 min.

These $\{P', f\}$ curves on quiet days exhibited ledges on the *E* region such as Halliday⁽⁴⁾ has observed. It was noticed that the occurrence of very weak traces of abnormal ionization in the *E* region, producing but very small variations in penetration frequency, in general rendered these ledges unobservable. Only those days were later classed as quiet for which these ledges appeared to vary smoothly and regularly throughout the day. We are fairly satisfied that, with one exception (16 July), the early observations would have been classed as quiet on this basis. On one occasion (6 November) a single persistent layer of weak abnormal ionization at a height of 100 km. was observed which did not correspond to the vanishing or obscuring of the ledges. Here the criterion was insufficient to exclude a case in

which an abnormal influence was undoubtedly present. The care described here in the classification of days was taken because results for even slightly disturbed days were found to be very different from those for quiet days, as will be shown later when we discuss the results for 6 November.

Except that observations of *E*-region penetration, each occupying about 10 min., were made at intervals of 30 min., measurements of amplitude were obtained continuously throughout the period from midday to sunset. The absorption-measurements were stopped in the evening when the reflection coefficient became

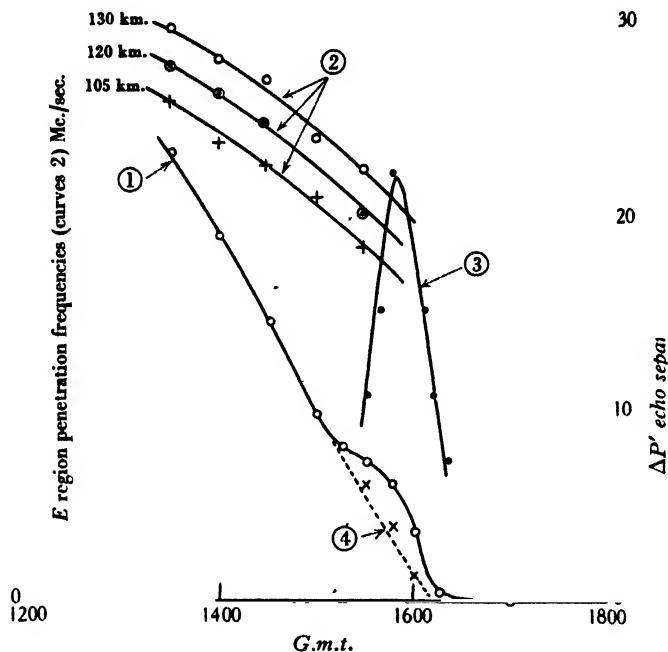


Figure 2. Results on 30 November 1936. Frequency, 3.22 Mc./sec.

so great that its difference from unity could not be measured, and the *E*-penetration measurements were stopped when the frequency approached the broadcasting band.

Although experiments were started on a large number of days the results were not used, for the purposes of this paper, unless throughout the day the *E*-region behaviour satisfied the condition of quietness previously explained. This limits the results to 12 days, distributed fairly evenly throughout the interval between 5 June and 2 December 1936.

The results of a typical day's experiments are given in figure 2, which shows the observed reflection coefficient (1) and the *E*-region penetration frequencies (2), each as a function of time of day.* Each point on the curve (1) represents the

* The *E* region on this occasion showed three penetration frequencies corresponding to equivalent heights of about 105, 120, and 130 km. The three penetration frequencies are shown in the figure.

mean of about 20 observations taken during a period of 5 min. The curve (3) also shows the amount of the observed separation due to splitting of the F -region echo. This splitting arises from retardation in the F_1 region and corresponds to the portion $a-b$ of the $\{P', f\}$ curve shown in figure 1. The intensity-measurements were made on the more retarded echo (ordinary wave), and a correction was made in the following way to estimate the corresponding absorption in the F_1 region. It was assumed that the path-difference between the two echoes was entirely due to group retardation in the F_1 region, and that the extra absorption would be given by

$$\Delta(\log \rho) = -\frac{\nu}{2c} \Delta P',$$

where ρ is the reflection coefficient, $\Delta P'$ is the group retardation, and ν is the collisional frequency in the F_1 region⁽¹⁾. The value 3×10^8 per second was taken for ν , and the absorption then calculated was used to correct the observed reflection coefficient as shown in curve (1) of figure 2. The corrected portion of the curve is marked (4). The fact that it appears to be a smooth prolongation of the uncorrected portion of curve (1) indicates in the first place that the hump in the observed curve is in fact due to F_1 -region retardation, and in the second place that the value chosen for ν is roughly correct.

§ 3. THEORETICAL CONSIDERATIONS

In the following discussion:

c is the velocity of light,

e the charge on the electron (e.s.u.),

h the distance above the ground,

H the earth's magnetic field,

H_L the vertical component of the earth's magnetic field,

H the scale height of the atmosphere,

I the number of electrons produced per cm^3 per second by an ionizing agency,

κ the absorption coefficient,

m the mass of the electron,

N the number of electrons per cm^3 , and p the pulsance of the wave,

$p_H = He/mc$ and is the gyromagnetic pulsance,

$p_L = H_L e/mc$ and is the longitudinal gyromagnetic pulsance equal to $1.21 \times 2\pi \cdot 10^6$,

$p_0 = \sqrt{(4\pi Ne^2/m)}$ and is the penetration pulsance for a region with maximum electron-density N ,

$x = h/H$ and is the height measured in terms of the scale height of the atmosphere,

α is the recombination coefficient,

β the attachment coefficient,

θ the angle between the vertical and the earth's magnetic field,

μ the refractive index,

ν the collisional frequency of the electrons,

ν_0 the value of ν at the ground, and ν_m the value of ν at the level of maximum ionization.

ρ is the reflection coefficient of the wave, equal to $\exp(-2\int \kappa dh)$ where the integral is taken over the path of the wave in the ionosphere,

ρ is the density of the atmosphere and χ the sun's zenith angle.

In attempting to explain the absorption-measurements we shall assume that all the absorption occurs in the E region.* We shall also assume that the E region is produced by the incidence of a monochromatic ionizing radiation on an atmosphere with an exponential gradient of density (i.e. a homogeneous isothermal atmosphere) and that the loss of electrons is due entirely to a recombination process, so that the rate of loss is proportional to N^2 . The coefficient of recombination will be assumed to be constant throughout the region. This type of E region has been discussed by Chapman⁽⁵⁾ and we shall call it a *Chapman region*. In the type of atmosphere which we have assumed the frequency of collision between electrons and molecules will vary exponentially with height.

In calculating the total absorption of a wave reflected from the F region we start with the expression⁽⁶⁾

$$\kappa = \frac{1}{2c} \frac{4\pi e^2}{m} \frac{N\nu}{(p \pm p_L)^2 + \nu^2} \frac{1}{\mu}.$$

We next assume that the value of μ for the wave as it passes through the E region is approximately unity, since the wave-frequency concerned was always sufficiently large compared with the penetration frequency of the E region. The absorption coefficient for the ordinary wave at any height is now seen to be given by

$$\kappa \propto \frac{N\nu}{(p \pm p_L)^2 + \nu^2} \quad \dots\dots(1).$$

We shall investigate the variation of the numerator and the denominator of this expression separately. Let us assume first that the ionization is in equilibrium with the ionizing agency so that we have

$$N \propto \sqrt{\frac{I}{\alpha}}.$$

From Chapman's analysis we have

$$I = B \exp \{-x - C \sec \chi \exp(-x)\},$$

where B and C are constants.

We have assumed an exponential variation of the collisional frequency, so that we have also $\nu = \nu_0 \exp(-x)$. These assumptions give

$$N\nu = \nu_0 \sqrt{\frac{B}{\alpha}} \exp \left\{ -\frac{3x}{2} - \frac{C \sec \chi}{2} \exp(-x) \right\}.$$

This expression for the numerator in equation (1) has a maximum at a distance x' below the ionization maximum, where $\exp(x') = 3$, corresponding to a distance $1.1H$ below the ionization maximum. The forms of the ionization curve and of the curve for $N\nu$ are shown in figure 3.

* It is assumed that the correction mentioned in § 2 has been made for F_1 -region absorption.

In integration through the absorbing region to calculate the total absorption, the most important contributions will arise from those regions near the maximum for $N\nu$ and if, at these places, $(p+p_L)^2 \gg \nu^2$ then the variation of ν in the denominator of (1) can be neglected.

We can show that this approximation is legitimate by considering the fact, stressed by Appleton⁽⁷⁾, that the measurements of penetration frequency show the propagation at the E -region maximum to be quasi-transverse in character, so that $(\sin^2 \theta/2 \cos \theta) p_H \gg \nu$ at these levels. This gives $\nu \ll 6.5 \times 10^5$ at the E -region maximum, and hence $\nu \ll 1.95 \times 10^6$ at the level of maximum $N\nu$. For the waves used in the present absorption-measurements p is of the order of 2.5×10^7 per

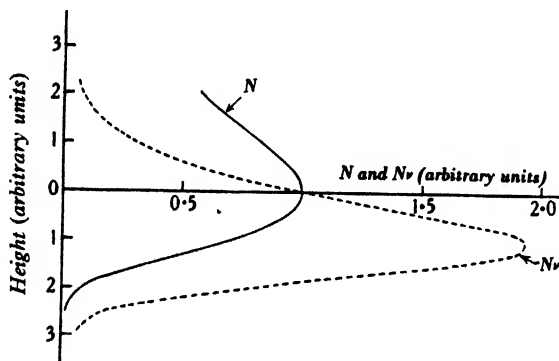


Figure 3

second, and it appears certain that $(p+p_L)^2 \gg \nu^2$ at the height considered. We therefore replace

$$\frac{N\nu}{(p+p_L)^2 + \nu^2}$$

by

$$\frac{N\nu}{(p+p_L)^2}$$

in expression (1).

We are now in a position to integrate the absorption of a wave in going right through the E region and returning after reflection from the F region and we have

$$\begin{aligned} -\frac{1}{2} \log \rho &= \int_0^\infty \kappa dh \\ &= \frac{4\pi e^2}{2cm(p+p_L)^2} \int_0^\infty N\nu dh \\ &= \frac{1}{2cm(p+p_L)^2} \nu_0 \sqrt{\frac{B}{\alpha}} \int_0^\infty \exp \left\{ -\frac{3}{2} \frac{h}{H} - \frac{C \sec \chi}{2} \exp \left(\frac{-h}{H} \right) \right\} dh \quad \dots\dots(2). \\ &= \frac{1.25}{c} \frac{4\pi e^2}{m(p+p_L)^2} H\nu_0 \sqrt{\frac{B}{\alpha}} \left(\frac{\cos \chi}{C} \right)^{1.5} \quad \dots\dots(3).* \end{aligned}$$

* See Appendix

This expression shows that the integrated absorption varies with the sun's zenith angle in such a way that

$$-\log \rho \propto (\cos \chi)^{1.5} \quad \dots\dots(4).$$

It is next of interest to calculate expressions for the total absorption in the cases where electrons are lost either (a) by attachment to neutral molecules, or by (b) recombination, the recombination coefficient α varying proportionally to the molecular density.* It is first to be noted that in each of these cases no maximum of ionization density could be formed by any radiation whose ionizing power decreased as it passed through the medium. This has previously been pointed out by Appleton & Naismith⁽⁸⁾ for case (a). It is equally true for case (b), as can be seen by noting that the rate of production of ions is proportional to the molecular density ρ and to the ionizing power of the incident radiation I , whereas the rate of loss of electrons is proportional to ρN^2 , since the recombination coefficient is itself proportional to ρ . Hence, under equilibrium conditions $\rho I \propto \rho N^2$ or $N^2 \propto I$, and since I decreases steadily as the radiation penetrates more deeply there can be no maximum in N .

Appleton & Naismith⁽⁸⁾ have recently given reasons for believing that the E region is produced by ultraviolet light and is governed by a recombination process, so that the above arguments apply to it. It therefore follows that the coefficient of recombination α is independent of pressure at the levels concerned. It is generally supposed⁽⁹⁾ that α is proportional to pressure up to a height of about 80 km. and then becomes independent of pressure, which is in agreement with the above deduction.

If maxima of ionization are observed considerably lower down, either they must be due to ionizing agencies whose ionizing power does not decrease as they penetrate (e.g. corpuscles), or the limiting pressure at which the recombination coefficient has usually been supposed to become constant must be considerably in error.

Returning now to the calculation of total absorption in the case where electron-loss is either by attachment or by recombination with α proportional to density, we notice that, although a maximum of ionization cannot occur in either of these cases, there will be a maximum in the value of $N\nu$ so that, for the reasons given in the discussion of equation (1), there will be a level at which the absorption is a maximum and the absorption coefficient integrated to infinity will be finite.

If we now assume that the ionization maximum occurs in a region where α is independent of density but that the absorption occurs a little lower down, where the processes of electron-loss are assumed to be either attachment, or recombination with α proportional to pressure (the increasing pressure will make both these processes more likely lower down), we can perform calculations similar to those given earlier in this section. We shall not give the calculations in detail but merely outline them first for the case of attachment and then for that of recombination.

* Theories of recombination based on three-body processes require α to be proportional to pressure, and for an isothermal atmosphere this is the same as being proportional to density.

Attachment. $I = \beta \rho N$ for equilibrium

$$\begin{aligned} \text{hence} \quad N &= \frac{I}{\beta \rho} \\ &= \frac{B \exp \{-x - C \sec \chi \exp(-x)\}}{\beta \rho_0 \exp(-x)} \end{aligned}$$

$$\text{and} \quad N\nu = \frac{B\nu_0}{\beta \rho_0} \exp \{-x - C \sec \chi \exp(-x)\}.$$

$$\text{Hence} \quad -\log \rho \propto \cos \chi \quad \dots\dots(5)^*.$$

Recombination with α proportional to density (and pressure). For this case we may write $\alpha = a\rho$.

Then for equilibrium $I = a\rho N^2$.

$$\text{Therefore} \quad N = \sqrt{\frac{I}{a\rho}} = \sqrt{\frac{B \exp \{-x - C \sec \chi \exp(-x)\}}{a\rho_0 \exp(-x)}}$$

$$\text{and} \quad N\nu \propto \exp \left\{ -x - \frac{C \sec \chi \exp(-x)}{2} \right\},$$

$$\text{which leads to} \quad -\log \rho \propto \cos \chi \quad \dots\dots(6)^*.$$

Equation (3) is left in a form involving the unknown intensity of the ionizing radiation. It is shown in the appendix that it is possible to transform it into the expression

$$-\frac{1}{2} \log \rho = \frac{2.06}{c} \frac{p_0^2}{(p + p_L)^2} H\nu_m \quad \dots\dots(7),$$

which involves the penetration frequency p_0 and other quantities which may be taken as known. As we have already pointed out, the assumption leading to expressions (5) and (6) do not explain the formation of the ionization maximum; it is therefore not possible to turn equations (5) and (6) into a form involving the penetration frequency of the region.

§ 4. COMPARISON BETWEEN THEORY AND EXPERIMENT

We have calculated the magnitude of the absorption coefficient as a function of the sun's zenith angle on the assumption that there is always equilibrium between the electron-production and dissipation processes. At first sight we should not expect equilibrium except near midday, but we shall nevertheless test whether the total absorption is proportional to some power of $\cos \chi$, in accordance with equations (3), (5) and (6), by plotting the observed values of $\log \log \rho$ against $\log \cos \chi$. The results are shown in figure 4, which represents 12 days between June and December 1936. The closeness with which the observed points lie on straight lines shows that the observed values of $\log \rho$ are proportional to some power of $\cos \chi$ and, if we exclude 16 July and 6 November, it appears that the power is very close to 1.5 as given by equation (3). We have mentioned in § 2 that the $\{P', f\}$ observations give some reason for rejecting both these days. It thus seems that the diurnal variation of

* See Appendix.

absorption can be explained on the assumption that α in the absorbing region is independent of pressure and that the ionization is at each instant in equilibrium

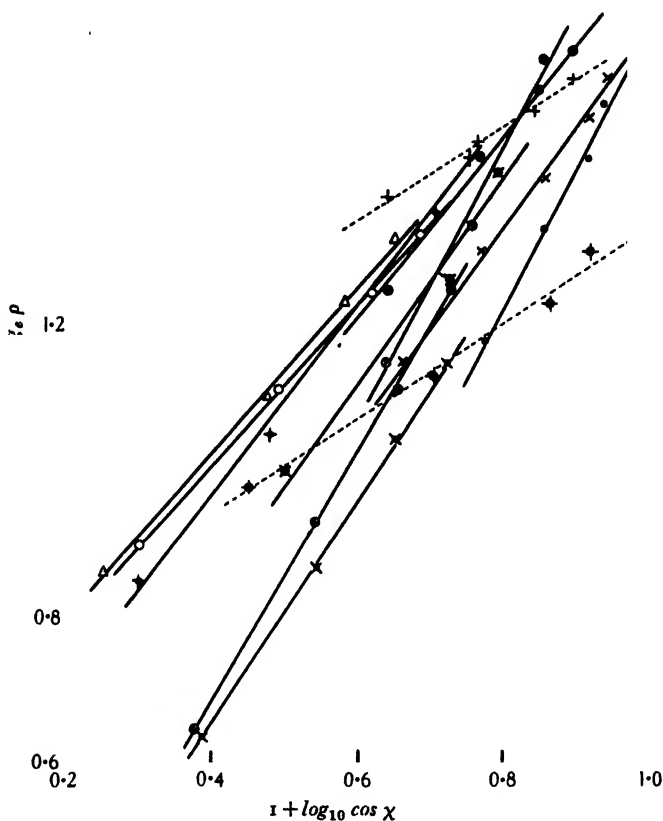


Figure 4

Symbols in figure 4	Date (1936)	Frequency (Mc./sec.)	Mean slope of curve
•	5 June	4.16	2.0
×	8 June	4.16	1.4
⊙	13 July	3.75	1.9
+	16 July	3.95	0.65
⊗	17 July	3.95	1.35
⊕	13 October	4.14	1.7
×	16 October	3.36	1.5
○	21 October	3.30	1.1
Δ	28 October	3.45	1.15
◆	6 November	3.45	0.7
⊠	30 November	3.22	1.45
+	2 December	3.22	1.25

Mean slope excluding 16 July and 6 November: 1.48.

with the ionizing agency. We shall discuss the significance of this equilibrium in the next section.

If the electrons were lost in the absorbing region by a process of electron-capture, or by recombination with α proportional to pressure, equations (5) and (6) show that we should expect $\log \rho$ to be proportional to $\cos \chi$ so that the slope of the lines in figure 3 would be 1 instead of 1.5. If, further, the ionization lagged behind the ionizing agency, we should expect an even slower variation of $\log \rho$ with $\cos \chi$. It appears from the experimental results that we must discard both these possibilities.

In his Bakerian Lecture to the Royal Society, Prof. Appleton⁽³⁾ described experiments in which the absorption of a wave of frequency 4 Mc./sec. was measured at midday throughout a period of 2 years. He compared the absorption with the corresponding value of the sun's zenith angle and found during the summer months that $\log \rho$ was approximately proportional to $(\cos \chi)^{\frac{1}{2}}$. In comparing the ratio of the summer to the winter noon values of $\log \rho$ he found, however, a marked disagreement with the simple theory. He considered that this discrepancy might possibly be due either to the influence of region- F_1 absorption in winter, or to the absorbing influence of a stratum below region E in which ν was not negligible in comparison with p , so that the variation of attenuation with change of χ was not so rapid as it is in the case of region E . Our diurnal curves for quiet days, however, appear to fit the $(\cos \chi)^{\frac{1}{2}}$ law both in summer and in winter, and it is difficult to reconcile the two results.

We have seen that equation (3) gives the right form of variation with the sun's zenith angle, so we now turn to equation (7), which is derived from equation (3), and consider whether the observed absolute value of the reflection coefficient agrees with our knowledge of the magnitude of the other quantities. We shall take the results of figure 2, which give, at 1400 G.m.t.

$$\begin{aligned}\log \rho &= -1.85, \\ p_0 &= 2\pi \times 2.75 \times 10^6 \text{ sec}^{-1}, \\ p &= 2\pi \times 3.22 \times 10^6 \text{ sec}^{-1},\end{aligned}$$

and hence, from equation (7) $H\nu_m = 3.5 \times 10^{10}$ cm./sec. In this calculation we have taken the greatest of the three penetration frequencies which were observed on this occasion; the equivalent height of the corresponding region was about 130 km.* To see whether the calculated value of $H\nu_m$ is reasonable we take Martyn and Pulley's⁽¹⁰⁾ suggested values for the E region, viz.: $H = 9.05$ km. and $\nu = 3 \times 10^5 \text{ sec}^{-1}$, giving $H\nu_m = 27 \times 10^{10}$ cm./sec. This appears to be too large, and would lead to a value of $\rho = e^{-14.3}$, which is much too small. It is interesting to see what result we get if we take the simple theory as correct and use the observed value of ρ to give a value of ν_m assuming that $H = 9$ km. in the E region. We then arrive at the value $\nu_m = 3.9 \times 10^4$ per second, considerably lower than Martyn and Pulley's value. This is the value at the level of maximum ionization, around 130 km. If we adopt a previous suggestion of Martyn⁽¹¹⁾, that $\nu = 10^6$ at 90 km., then with $H = 9$ km.

* The heights here quoted cannot be measured more accurately than within about ± 5 km., partly on account of instrumental inaccuracy and partly on account of group retardation in the E region.

we should have $\nu = 1.2 \times 10^4$ at 130 km. which is not very different from our value. The value given here is also in agreement with some values given in his Cambridge Ph.D. thesis (not published) by F. T. Farmer, who used the group-retardation method previously described⁽¹⁾ and obtained a mean value of $\nu = 10^4 \text{ sec}^{-1}$ at a height of 130 km. We consider that a value of about 2×10^4 cannot be far wrong at 130 km.

In comparing this value of ν with that suggested by other workers for the *E* region we first draw attention to the fact that, if $H = 9$ km. near the *E* region, the value of ν is changing rapidly with height in this neighbourhood, so that it is important to specify the exact height when quoting a value for ν . We have mentioned that our value applies to a height of about 130 km., the level of maximum ionization at midday in midwinter; calculation and observation show that the level of maximum ionization at midday in summer is about 120 km., and 5×10^4 is the appropriate value for the collisional frequency. We have previously mentioned that the level of maximum absorption is at a distance $1.1H$ below the level of maximum ionization, so that the values of ν at this level would be 4.5×10^4 in winter and 1.5×10^5 in summer. When we remember that the value 3×10^5 given by Martyn and Pulley⁽¹⁰⁾ as "the mean value at the level of the *E* region" is based on absorption measurements, so that it represents the lower portion of the *E* region, it does not seem to be in serious conflict with the values given above.

§ 5. CONCLUSIONS

It appears to be possible to explain the experimental results regarding the absorption of waves, reflected under quiet conditions from the *F* region, by assuming that when the waves are not retarded by being near *F*-region critical frequencies, the absorption takes place in an *E* region which is of the Chapman form, i.e. a region in which the electrons are produced by homogeneous electromagnetic radiation incident from the sun, and the electron dissipation process is one of recombination with α independent of the pressure. This supposition requires that α must remain independent of the pressure down to levels about 12 km. below the *E*-region maximum.

An important point in the explanation outlined above is that the ionization throughout the absorbing region appears to be in approximate equilibrium with the ionizing agency over quite a large portion of the day. This means that in the equation

$$\frac{dN}{dt} = I - \alpha N^2$$

both I and αN^2 are large compared with dN/dt . Taking the values calculated from the observed absorption curves for 1600 G.m.t. in winter, and assuming that the appropriate value of N is that which would be calculated for the level of maximum N , i.e. $1.1H$ below the level of maximum N , we find that α must be at least 10^{-8} . This value is considerably larger than that, 2×10^{-10} , calculated by Chapman⁽¹³⁾ for recombination between electrons and positive ions at those pressures for which α is independent of pressure.

We have arrived at this same conclusion from a study of the diurnal variation of *E*-region penetration frequencies⁽²⁾; in that connexion the conclusion is valid only for the level of maximum ionization in the *E* region, but the present work shows it to be true lower down. The same deduction has been made for the level of the *E*-region maximum by Prof. Appleton in his recent Bakerian Lecture⁽³⁾.

In connexion with the results recorded in this paper it is interesting to recall an observation made by F. W. G. White⁽¹²⁾, who pointed out that in the afternoon and evening the absorption of waves decreases more rapidly than would have been deduced from a simple Chapman region. The reason for this is now seen to be that he was considering a Chapman region with too small a value of α , arrived at by observations on the nocturnal decay of the ionization maximum. We have given reasons elsewhere⁽²⁾ for supposing that the value of α in the daytime is greater than at night.

§6. ACKNOWLEDGEMENTS

In conclusion we wish to record our very great indebtedness to our colleagues who gave valuable help with the observations. Our thanks are due especially to Dr F. T. Farmer, and also to Mr K. G. Budden and Mr K. Weekes.

APPENDIX

We here take up some mathematical points referred to in the body of the paper.

(i) For the Chapman region given by

$$N = \sqrt{\frac{B}{\alpha}} \exp \left\{ -\frac{x}{2} - \frac{C \sec \chi}{2} \exp(-x) \right\},$$

the maximum of ionization occurs at a height x_m given by

$$\exp(x_m) = C \sec \chi \quad \dots\dots(a),$$

and the maximum value of N at this level is

$$N_m = \sqrt{\frac{B \exp(-\frac{1}{2})}{\alpha (C \sec \chi)^{\frac{1}{2}}}} \quad \dots\dots(b).$$

(ii) Equation (2) involves the integral

$$\int_0^{\infty} \exp \left\{ -\frac{3}{2} \frac{h}{H} - \frac{C \sec \chi}{2} \exp \left(-\frac{h}{H} \right) \right\} dh.$$

Write $\frac{h}{H} = x$ and we have

$$H \int_0^{\infty} \exp(-x) \exp \left\{ -\frac{C \sec \chi}{2} \exp(-x) \right\} \exp \left(-\frac{x}{2} \right) dx.$$

Now write $\frac{1}{2} C \sec \chi = k$ and $Z = \sqrt{k} \exp(-\frac{1}{2}x)$, and the integral becomes

$$\begin{aligned} H \int_{z=\sqrt{k}}^{z=0} \frac{Z^2}{k} \exp(-Z^2) \left(-\frac{2}{\sqrt{k}} \right) dZ \\ = H k^{-\frac{3}{2}} \left[Z \exp(-Z^2) - \int \exp(-Z^2) dZ \right]_{Z=\sqrt{k}}^{Z=0} \quad \dots\dots(c). \end{aligned}$$

Now x_m is known to be of the order of 12 so that, from equation (a),

$$C \sec \chi = 2k \approx e^{12};$$

hence

$$\sqrt{k} \approx 280.$$

The first term in equation (c) is thus approximately zero at both limits; the second term is the error-function integral taken between the limits 0 and 280, which, from tables such as those given by Jeans in his *Dynamical Theory of Gases*, are seen to be effectively the limits 0 and ∞ which give the value $\sqrt{\pi}/2$. The integral is therefore equal to

$$\frac{1}{2} \sqrt{\pi} H \left(\frac{2}{C \sec \chi} \right)^{1.5} = 2.5 H \left(\frac{\cos \chi}{C} \right)^{1.5},$$

which leads to equation (3).

(iii) If in equation (3) we substitute the value of N_m as given by (b) and then convert to the penetration frequency p_0 as given by

$$p_0^2 = 4\pi N_m e^2 / m,$$

and also substitute

$$\nu_m = \nu_0 \exp(-x_m) = \frac{\nu_0}{C \sec \chi}$$

from (a), we obtain

$$\frac{1.25 \exp(\frac{1}{2})}{c} \frac{p_0^2}{(p + p_L)^2} H \nu_m = \frac{2.06}{c} \frac{p_0^2}{(p + p_L)^2} H \nu_m,$$

which is equation (7).

(iv) Expressions (5) and (6) involve the integral

$$\int_0^\infty \exp\{-x - k \exp(-x)\} dx,$$

where

$$k = C \sec \chi.$$

This integral is

$$-\frac{1}{k} \left[\exp\{-k \exp(-x)\} \right]_0^\infty \approx \frac{1}{k} = \frac{\cos \chi}{C},$$

when k is large.

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A COMPARISON OF THE MIXED-POWDER AND SUBSTITUTION METHODS IN THE QUANTITATIVE EVALUATION OF X-RAY REFLECTIONS FROM CRYSTALLINE POWDERS

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ABSTRACT. The conditions determining the quantitative measurement of X-ray reflections by the substitution and by the mixed powder methods are compared with regard to the evaluation of atomic scattering factors. The paper is supplementary to a paper by Brindley and Spiers; it contributes particularly to the discussion of particle-size, of extinction, and of differential absorption. A method is indicated for determining the presence of differential absorption and so avoiding errors which may arise from that cause when the mixed-powder method is applied to coarse particles. Techniques are described relating to the substitution and to the mixed-powder methods. Attention is drawn to a technique in which the mixed-powder and substitution methods are used conjointly.

§ 1. INTRODUCTION

MESSRS BRINDLEY AND SPIERS have kindly given me the opportunity of reading the MS. of their paper on "The measurement of the intensities of X-ray reflections from crystalline powders in absolute units"⁽¹³⁾, the main subject of which is a comparison of the merits of the mixed-powder and of the substitution methods, and invite me to set out in a separate note those points on which my own experience leads to additional remarks. I gladly fall in line with this proposal in order that the two papers may conjointly provide an account of the technique which we have found effective in our work.

The more general aspects concerning the quantitative evaluation of intensities of X-ray reflections from powders have been dealt with by me in a short paper⁽¹⁾ related to some work of Schäfer. I may be allowed to refer to this paper so as to avoid repetition; Brindley and Spiers also discuss these points in so far as they are more directly connected with the comparison of the two methods and come to largely similar conclusions. Any difference in our views does not concern these more general aspects, but rather the practical application of different techniques. These points are perhaps best represented by reference to the successive development of the methods.

§ 2. GENERAL SURVEY

The first comprehensive discussion of the experimental conditions affecting intensity measurements was given with the classical measurements of the intensities of X-ray reflections from single rock-salt crystals by Bragg, James and Bosanquet

(reference to the various papers can be found in Bragg^(a)), when two points arose requiring particular attention. One was the establishing of the correct relation between the incident and the reflected beam having regard to absorption, the other was the correct allowance for the extinction effects which arise when the crystal units or crystallites composing the mosaic crystal exceed a certain size. With the aim of eliminating such errors the writer resorted to extremely fine powders constituted of such small particles that the maximum size of the crystallites imposed by the particle-size fell below the limit at which extinction effects arise. By using powders instead of single crystals the intensities of reflections became much weaker, and while in the experiments of Bragg, James and Bosanquet a direct comparison of the intensities of the incident and reflected beams could be made by means of a sensitive ionization method, with the much weaker reflections from powders a direct comparison did not seem practical. We therefore did not attempt to obtain absolute values of atomic scattering factors, but limited the problem to comparative measurements, a procedure which was generally adopted in later work. At first, we made use of a standard powder which could be inserted in the direct beam for given intervals of time, so that its reflections could be used as a measure of its intensity. The evaluation of the atomic scattering factors does then still require the allotment of the correct absorption coefficients to the powder specimens. We abandoned, therefore, this method in favour of the mixed-powder method⁽³⁾, in which fine powders of the substances to be compared are mixed in a known weight-ratio, when the same absorption coefficient, which does not require to be known explicitly, applies to the reflections from both substances, provided the powders are so fine that the absorption in the individual particle has a negligible effect on the reflected intensity. This it has when the particle-size is chosen so as to eliminate extinction effects and the required condition was therefore satisfied in our measurements⁽¹⁰⁾. Glocker and Schäfer⁽⁴⁾ applied the mixed-powder method to coarser powders, assuming that the particles were constituted of sufficiently small crystallites to avoid extinction errors, without giving consideration, however, to the fact that the assumption of a common absorption coefficient no longer held good and that any difference in the absorption coefficients of the substances affects the reflected intensities. An error arises then, owing to the fact that in a coarse powder mixture the X-rays reflected from particles of both one and the other substance travel on the average for a predominant part of their path in that substance. For the convenience of the present discussion we call this effect the "differential absorption effect". Schäfer in a subsequent paper⁽⁵⁾ has discussed in detail the errors involved.* Bradley⁽⁶⁾ has avoided the necessity of preparing fine powders by alloying the elements to be compared. Coarse particles of the alloy can then be used. The method is restricted to the comparison of those elements which can be alloyed to form crystallites with a common lattice and other limitations are imposed, but it eliminates in a very elegant way the extinction and absorption errors of coarse particles. Brindley and Spiers⁽⁷⁾ avoid the effects of differential absorption (not those of extinction) encountered with large particles, by resorting to separate layers and

* See also reference (10).

exposing them in succession, in which case, as we have indicated above, the absorption coefficient for each layer must be known. They give a detailed analysis of this procedure which originally they called "the method of separate layers". With the fine particles satisfying the condition of negligible extinction used in our work, the differential absorption effect does not arise, as the limitation imposed in order to avoid extinction restricts the size of the particle more than is required for avoiding absorption. In increasing the accuracy of measurement the writer, in collaboration with Baxter, was, however, faced with a particular source of error resulting from the superposition of lines on background steps and on other lines^(11, 12). Such superpositions occur with the reflection lines of one single substance; they increase in number, however, with the number of lines and are thus reduced when the reflections of the two substances are recorded separately.

The writer was thus also induced to resume the separate recording of the reflections from the two substances placed alternately in the camera, a procedure for which we used the term "substitution method", a term adopted in their recent paper also by Brindley and Spiers. Their work was entirely independent of ours and had also different aims, as they were primarily interested in separating the layers so as to avoid the necessity of preparing fine particles and intimate mixtures of powders, while we were mainly concerned with obtaining separate records of the lines and background steps of the two substances so as to avoid superpositions.

It will be seen from this survey that the development of intensity-measurements is not in the direction of evolving one general method, but rather of developing a number of specialized techniques adapted to particular conditions. In fact, so long as we are unable to prepare in a general way particles of controlled sizes or particles constituted of small crystallites and to introduce into the calculation sufficiently accurate values for the absorption coefficients, only limited groups of substances are accessible to intensity-measurements, and separate consideration has to be given to each individual case.

A few specific points may be discussed, having regard in the first place to the evaluation of atomic or unit-cell scattering factors. Such determinations require the elimination of any influence of the particular habitus of the reflecting crystallites, i.e. of extinction effects and also of all effects of absorption.

§ 3. PRIMARY EXTINCTION

Primary extinction becomes appreciable for crystallites, the term being used in the sense of the extension of a regular lattice block, exceeding 100 or 1000 atom layers according to the atomic weights of the elements constituting the crystals. This corresponds to magnitudes of the crystallites of the order of $5 \cdot 10^{-5}$ or $5 \cdot 10^{-4}$ mm. Such small crystallites may be secured either by actually reducing the size of the particles to these limits or with coarser powders if the particles are adequately subdivided into smaller crystal units. In our experience such a state of subdivision cannot be presumed to exist, and while a large mosaic crystal is generally subdivided into much smaller crystallites we are not justified in assuming that the size of such crystallites decreases at the rate at which the overall size of the crystal particles

becomes smaller, the habitus of the crystallites being rather not to break into smaller units after a certain limit is reached.

To quote two typical instances the writer observed for rocksalt and for copper, which can be taken as representatives of the soft, imperfect and of the ductile types of crystals and for which it might be expected that the breaking up of particles into very small crystallites will most readily take place, quite appreciable extinction effects even after violent mechanical action, so long as the particles themselves exceeded the limits above which the individual crystallites would give extinction effects. This indicates that the individual crystallite was of the same order of magnitude as the crystal particle. Similar observations were made by other experimenters.

We certainly do not wish to say that coarser particles of a powder are never subdivided into such small crystallites as to be free from extinction, but it appears that such a condition cannot be presumed to exist without having actually been ascertained for each particular powder. Such a verification can be carried out in two ways: either by determining the intensities of a number of lines and comparing these with the normal intensity-distribution of the substance and so revealing extinction effects by systematic differences of the intensity-distribution (such an evaluation requires that the scattering properties and temperature factors of the substance shall be already well known), or by comparing the relative intensities of the lines with those obtained from a preparation of the same substance known to be so fine as to be free from extinction. In this case a fine powder must actually be available.

§ 4. ABSORPTION AND SECONDARY EXTINCTION

Absorption coefficients have been determined experimentally for a number of substances; in a more general way they can be derived from expressions established by Jönsson⁽⁸⁾. Brindley and Spiers, in advocating the use of the substitution method, suggest obtaining the necessary absorption coefficients of the substances constituting the separate layers from Jönsson's expressions. Comparing the absorption coefficients so derived with experimental values so far as such data are available, for instance the values collected in Compton and Allison's book⁽⁹⁾, the agreement is far from uniform; we do not feel sure, therefore, whether these expressions can be considered as sufficiently reliable until they have found a fuller theoretical basis. Any uncertainty on this point should not, however, constitute an objection against the substitution method, as it can be safely assumed that within a short time sufficient experimental material will be available either to confirm or to modify Jönsson's expressions and so to make definite values available. A difficulty of a different kind appears, however, in applying these data. The intensity of the X-ray beam is reduced more than by normal absorption when it encounters crystallites oriented at a reflection angle with regard to the beam. Such a secondary extinction effect appears as an addition to the coefficient of true photoelectric absorption. For the case of a fine powder with crystallites oriented at random this entails an addition to the normal absorption which is of comparatively little signi-

ficance. The effect becomes much more important, however, for coarser powders, in which the individual crystallites even when small are arranged as a mosaic approximately parallel one to another. The addition to the normal absorption coefficient introduced by secondary extinction deserves then closer attention, as it is peculiar to each individual powder and assumes different values for different reflections. Further, in our experience some binding or spacing material must in general be added to the powder, which besides fixing the powder in its holder has the important function of preventing preferential orientation, which occurs when the powder is pressed in the frame or cavity in which it is held. This binding material adds to the absorption, particularly with substances of small atomic weight. Brindley and Spiers do not discuss the effects of secondary extinction and of the binding material on the absorption coefficient. There are certainly instances when they do not arise, namely, with hard particles constituted of small crystallites arranged in a micro-crystalline random orientation, which cannot be affected by outside agents. Secondary extinction is then small, and a binding material can be dispensed with. In general, however, the addition of a binding material seems necessary and the modification of the normal absorption coefficient introduced by it and by the secondary extinction effect of mosaics must be taken into account when the substitution method is being used.

§ 5. THE TWO METHODS COMPARED

Comparing the merits of the substitution and the mixed-powder methods, we may say that the most prominent advantage of the first seems to be that it can be applied to coarse particles, its disadvantage that it requires explicit knowledge of the numerical values of the absorption coefficients of the powders.

From what we have discussed in §§ 3 and 4, it will be seen that correct values of scattering factors can only be obtained if errors due to extinction and to preferential orientation are eliminated. The practical way for ascertaining that this condition is satisfied requires that the substances shall be available in a state of fine powder, either for using such a powder in the actual determination, or for providing the means of verifying by comparison that for the particular substance larger blocks are sufficiently subdivided and oriented at random. The substitution method does not, therefore, make accessible to quantitative evaluation of scattering factors the large number of substances of which no fine powders can be prepared; it can be applied to the limited group of coarse powders or aggregates from such substances for which it can be ascertained that they are constituted of sufficiently small crystallites and that these are oriented at random and not in the pattern of a more or less regular mosaic.

We tend, therefore, to view the problem of determining scattering factors or making absolute intensity-measurements in the first place as a problem of preparing sufficiently finely subdivided powders, and consider that powder methods should be used for accurate quantitative measurements only when such powders are available. In previous papers we have indicated the means by which fine powders can be

obtained; we found that they could be prepared by chemical processes of precipitation or of reduction but not by the mechanical action of crushing or grinding.

§ 6. POINTS OF TECHNIQUE

A few remarks may be made regarding points of technique which, in individual cases, may weigh in deciding in favour of one or the other method.

As regards the substitution method, it will be seen in each individual case whether sufficiently reliable absorption coefficients for the particular substances and wave-lengths are available and whether such values apply to the actual powder layer. Here we may indicate a method whereby one difficulty, encountered with our original design of powder-holder and also with the powder-holder described by Brindley and Spiers—that the powder must be mixed with binding material affecting the absorption coefficient or firmly pressed in a holder and so subjected to preferential orientation—can be eliminated by exposing it to X-rays behind a celluloid window or in a narrow celluloid tube, according to the type of camera used, the only essential condition being that the two powders to be compared should be placed behind windows giving equal absorption.

Regarding the method of mixed powders a limitation is imposed by requiring substances in the state of fine powders, but the preparation of an intimate mixture of particles of two substances presents no serious difficulty if a brittle spacing or mixing substance is used, in the way described by us elsewhere. In this connection it should be mentioned that there exists a definite criterion for ascertaining whether the particles of a mixed powder are sufficiently small or sufficiently well mixed. This consists in taking records from the mixture for two wave-lengths so chosen that the X-rays suffer widely different absorption, while avoiding those wave-length ranges for which the scattered intensities are much affected by anomalous dispersion. When the relative intensities of the reflections from the two constituents of the powder are then compared, any differential absorption error is distinctly shown by a change in the relative intensities of the lines obtained for the two wave-lengths. No equally direct test is available for deciding whether absorption coefficients have been correctly assessed or whether extinction effects have occurred.*

To illustrate the point by reference to the experiments quoted by Brindley and Spiers, it fully conforms with expectation that with the coarse particles errors of differential absorption should occur; at the same time we are not sure whether part of the deficiencies observed is not due to extinction. That mechanically prepared copper powders show marked extinction effects has been observed by the writer in the case of mixed layers of mechanically pulverized and chemically precipitated copper with nickel, any differential absorption effect being in these conditions small

* It should be noted—a point which does perhaps not appear so clearly from the discussion in § 5 of Brindley and Spiers's paper—that for the substances and wave-lengths generally used extinction sets a smaller limit to the permissible size of the crystallites than differential absorption sets to the size of the particles. When the crystallites are constrained by the particle size, the limitation set to the extension of the particles in view of extinction will thus also eliminate differential absorption. The converse relation cannot in general be assumed to hold good.

owing to the small difference in the absorption coefficients. The actual correct assessment of extinction by comparison of the intensities of reflection for varying orders or angles requires a very detailed knowledge of the change of scattering with angle and of the temperature factor.

When the mixed-powder method is used for larger particles it should be noted that any differential absorption effect very largely depends on the relative absorption coefficients of the two substances and disappears when the linear absorption coefficient is the same⁽¹⁰⁾. Such effects can thus be greatly reduced by choosing substances with nearly equal absorption coefficients. This technique makes it possible in selected cases to apply the mixture method to very coarse particles if such measurements are justified when regard is had to extinction.

In our experiments we had used aluminium as a comparison substance; owing to the small scattering factor of the aluminium atom comparatively large crystallites are free from appreciable extinction and so we can obtain strong aluminium reflections without much interference from extinction effects. Brindley and Spiers now recommend aluminium for general use. It should be noted, however, that we were able to use aluminium because our particles complied with the criterion of negligible extinction and therefore, *a fortiori*, were sufficiently small not to give rise to any errors of differential absorption; the reason why we preferred it was, in the first place, that it has no absorption edges in the range of wave-lengths usually used and introduces therefore no appreciable anomalous dispersion and no absorption steps.* Such effects need, however, only be considered in measurements of a high accuracy. Outside of such requirements, when it is desired to avoid differential absorption effects of larger particles it is preferable to choose a substance which has nearly the same absorption coefficient as the substance to be investigated, among the range of oxides and chemically reduced metal powders which are available in the state of sufficiently fine subdivision.

§ 7. OTHER DEVELOPMENTS

I take the title chosen by Brindley and Spiers for their paper as signifying that quantitative measurements of scattering factors are the subject under discussion. It is for this reason that I have dealt with these in the foregoing notes. Brindley and Spiers remark, however, that in previous papers I impose an unwarranted restriction by assuming beforehand that extinction effects should be avoided. The points in my papers to which these remarks apply are concerned as is the present discussion, with the measurement of scattering factors, and I think that for such measurements superpositions with extraneous effects should be excluded. There is certainly, however, a wide field for the substitution method outside of this particular domain;

* The aluminium used in our experiments was chemically prepared aluminium powder obtained from Kahlbaum; the ordinary aluminium powders prepared by mechanical processes are not suitable. Brindley and Spiers, experimenting at first with such powders, found that they were unsuitable and in a discussion expressed surprise that I could use aluminium powder for intensity-measurements until they obtained a sample of an aluminium powder from the same source. The point illustrates clearly the great importance of using suitable powders.

in fact while Brindley and Spiers developed and discussed the substitution method as a means of avoiding the necessity of preparing fine particles and intimate mixtures for the comparative determination of scattering factors, I myself at an earlier stage did not pursue the use of the method for determining scattering factors owing to the difficulty of assessing correct values for the effective absorption coefficients. I took it up again after having developed the method of mixed powders to meet problems which arose in connection with this method and as an auxiliary to it.

Two applications are here of particular interest. One is the comparison of corresponding reflections from different preparations of the same substance, when by comparing the shape and intensity of lines from preparation of different fineness we can ascertain whether the required state of subdivision has been attained. Instances of too imperfect powder particles or of vanishing size-distribution can so be found. In such comparisons, where both powders are constituted of the same substance, the correct assessment of the absorption coefficient is immaterial, so long as the same proportion of binding material is used in each case and the particles are sufficiently small in all the powers to avoid the occurrence of a differential absorption effect between this binding material and the particles. By using for one of the powders particles constituted of sufficiently large crystallites, we can obtain lines the width of which is only determined by factors other than the condition of the crystallites and thus distinguish any goniometer broadening from the broadening due to the imperfection of the crystallites. Another application is the use of the substitution method for obtaining separate records and the exact relative location of lines and background steps which on the record from the mixed powder are in too close proximity to be easily evaluated⁽¹²⁾. It is possible to determine from such separate records whether actual superposition has taken place, and in some cases to correct for superpositions from the intensity-distribution determined for each line. It is for this reason that the goniometer described in another paper⁽¹¹⁾ has been so designed that the two patterns of lines obtained by the substitution method are recorded under conditions securing as accurately as possible their correct relative position, this is done by taking the two records on adjacent strips of the same film held throughout in a rigid position with respect to the slit system of the goniometer.

In conclusion, attention may be drawn to one merit of the substitution method which has not been mentioned in the paper by Brindley and Spiers, namely, that in comparison with records from the mixed powders the lines stand out of the background more strongly. This does not reduce the interference of background steps we have discussed in other papers, as the whole of the powder instead of one part only contributes to one group of lines and to the regularly reflected part of the background, but it helps to make the lines more easily measurable.

We wish by no means to present the distinction between the two methods as a case of superiority of one over the other, and if we lay more weight than Brindley and Spiers on the precautions which have to be taken when the substitution method is applied to measurements with large particles, this is because we believe that the substitution method, by eliminating differential absorption, does not in itself eliminate other more subtle errors which account for many faulty investigations associated

with coarse powders, a point with which Messrs Brindley and Spiers will probably agree, but which should perhaps be stressed in the interests of those less familiar with the intricacies of intensity-measurements of X-ray reflections.

§ 8. ACKNOWLEDGEMENT

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SENSITIVITY OF PHOTOGRAPHIC PLATES IN THE REGION 2500–2000 Å.

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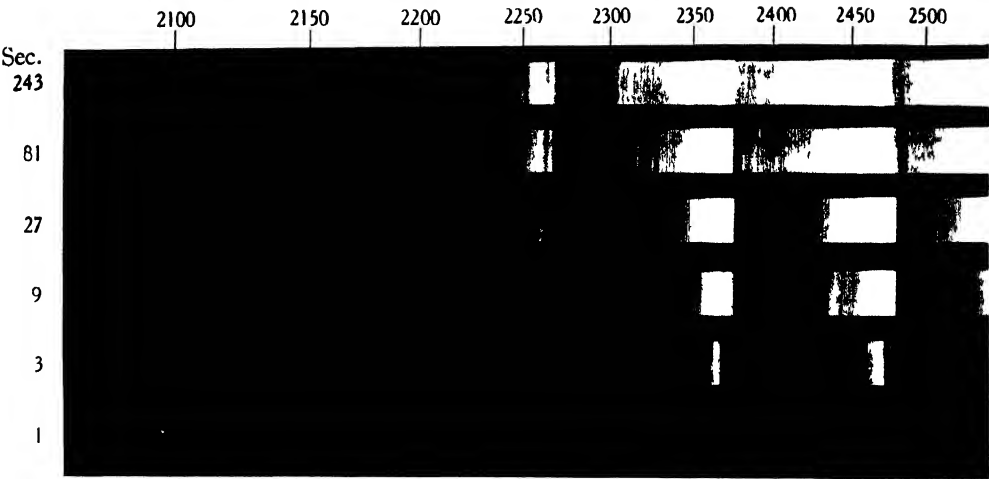
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ABSTRACT. The effect of sensitizing photographic emulsions for the wave-length region 2500 to 2000 Å. by bathing them in fluorescent substances before exposure, or by decreasing their gelatin content, is examined experimentally. The characteristics of seventeen different types of plates are compared by a simple method of sensitometry in which the plates are given stepped exposures to the γ bands of nitric oxide under reproducible conditions. Direct density-comparisons made by visual estimation are then sufficient to give the information as to relative sensitivities which is most likely to be required by the practical spectroscopist. Apart from the Ilford Q2 plate, which has special characteristics that are fully discussed, it is found that a measurable record can be obtained with the least possible exposure on an ordinary plate. In this sense, therefore, the methods of sensitization at present available do not have the effect which is generally ascribed to them. Their main use is for increasing contrast and saturation density, not threshold sensitivity. A table gives the relative threshold exposure times needed for the different plates at various wave-lengths, and spectrograms on representative plates are reproduced.

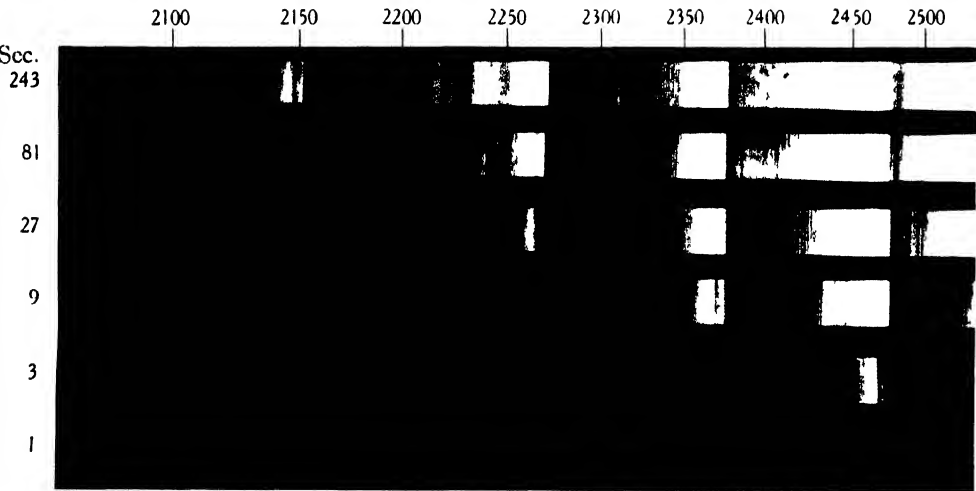
§ 1. INTRODUCTION

HAVING had occasion recently to photograph spectra of low intensity in the region 2500 to 2000 Å., we were surprised to find that more satisfactory results could be obtained with ordinary plates than with plates recommended as having much higher ultra-violet sensitivity. This paper presents the results of experiments made with a view of clearing up this apparently anomalous behaviour. The point of view throughout is that of the practical spectroscopist who wishes to photograph a spectrum in this region of the ultra-violet.

It is well known that the sensitivity of an ordinary photographic emulsion begins to fall rapidly just below 2500 Å., and is very low at 2000 Å. In the Schumann region the sensitivity becomes negligibly small. This fall is due, not to an intrinsic failure of the short-wave radiation to render developable the silver salts used in the emulsion, but to an increasingly strong absorption of the radiation by the gelatin of the emulsion. Thus in the Schumann region the halide grains are still photochemically active, but they are so completely screened by an opaque layer of gelatin that the emulsion is useless for photography. To radiation of wave-lengths 2500 to 2000 Å. the gelatin is not so opaque, and the effect is accordingly not so pronounced: an ordinary plate is still serviceable at 2500 Å. and can be made to yield traces at 2000 Å. Nevertheless, the results obtainable in this region are unsatisfactory in

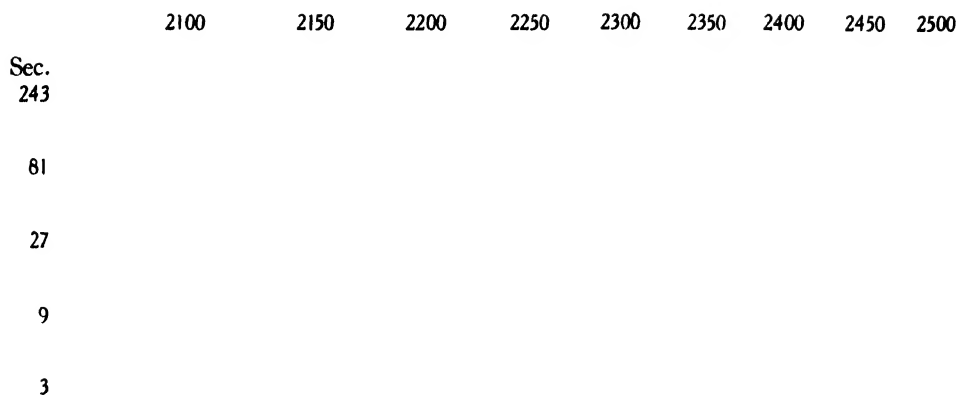


(1) Ordinary plate.

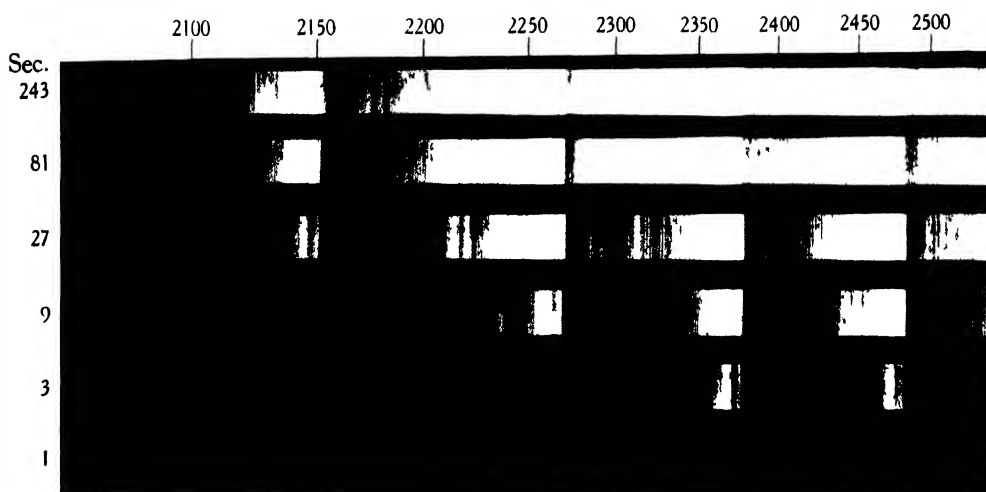


(2) Oiled ordinary plate.

Plate 1.



(3) Hilger Schumann plate.



(4) Ilford Q2 plate.

Plate 2.

comparison with those in the near ultra-violet, and many attempts have been made to combat the fall in sensitivity. These attempts are based on the assumption, obviously made with considerable *a priori* justification, that the photographic technique which has succeeded in vacuum spectroscopy will also be effective in increasing sensitivity in the region 2500 to 2000 Å. It is in fact commonly stated that this is indeed so^(1,2). Uncritical acceptance of such assertions without careful examination of their exact meaning, however, is, we believe, a source of widespread disappointment among spectroscopists, to whom this region is of great importance.

§ 2. TYPES OF SENSITIZATION IN PRESENT USE

In the Schumann region the loss of sensitivity mentioned above is commonly overcome in two ways. For the region 2500 to 2000 Å., too, the preparation of specially sensitive plates, whether in the laboratory or in the factory, is based on one of these methods.

(1) It may be arranged that the radiation shall have to pass through as little gelatin as possible before encountering the silver halide. Examples of this method are:

- (a) the original Schumann plates⁽³⁾, in which no gelatin is used;
- (b) the commercial Schumann plates (Hilger and Agfa), in which the gelatin-content of the emulsion is greatly reduced as compared with an ordinary emulsion;
- (c) the Duclaux-Jeantet plates⁽⁴⁾, in which the gelatin of an ordinary plate is removed by solution in sulphuric acid;
- (d) the Ilford Q plates⁽⁵⁾ in which a rock-garden effect is produced by the manufacturing process, the silver halide grains being concentrated on the surface of the gelatin.

(2) An ordinary plate may be bathed in a fluorescent substance which can convert the short waves into radiation able to penetrate the gelatin. Substances commonly used are:

- (a) mineral oils⁽⁶⁾ and greases⁽⁷⁾;
- (b) sodium salicylate⁽⁸⁾;
- (c) anthracene⁽⁹⁾;
- (d) commercial sensitizers, such as those used on special ultra-violet plates marketed by Eastman* and Agfa†.

In view of our disappointing experience with certain of the more usual of these devices for sensitizing, we decided to make a thorough test of plates representing each type.

§ 3. EXPERIMENTAL PROCEDURE

The method of testing is in essence as follows. Each plate was exposed to ultra-violet light (2500 to 2000 Å.) under standard reproducible conditions. It was then processed according to the manufacturer's recommendations. Finally, a direct

* Di-hydro-collidine, ethyl carboxylic ester.

† Messrs Agfa Photo, Ltd., inform us that the nature of the Agfa sensitizer is a manufacturing secret.

comparison was made, wave-length by wave-length, between the densities produced in this way on the several plates. The following discussion of the procedure adopted may perhaps be of interest.

Since the variation of plate-sensitivity with wave-length is so marked in this region, direct exposure to a source emitting radiation of a mixture of wave-lengths is useless. For the same reason the use of a monochromatic source would not yield enough information: a series of such sources would be necessary. The most satisfactory method is to disperse a mixture of wave-lengths into a spectrum, expose the different plates to this spectrum, and then make density-comparisons between the plates at corresponding points along the spectrograms. The spectrum used may consist of lines, bands, or a continuum. Of these, a band spectrum is to be preferred, since, unlike both a line spectrum and a continuum, it will usually exhibit a considerable range of intensity in a short range of wave-lengths; and, unlike a continuum, it will serve as its own wave-length scale. As for the source, arcs and sparks are not so easy to control as discharge tubes. After some trials with other sources, we finally decided on a heavy-current discharge tube⁽¹⁰⁾, through which passed a slow stream of air. This provides a steady source of the γ bands of nitric oxide, which extend throughout the region 2500 to 2000 Å.; see plate 1. The bands are characterized by strong, well-defined heads, with long branches slowly degraded in the direction of shorter wave-lengths. The range of intensity thus available makes this band system particularly suitable for comparison of plate characteristics in the ultra-violet. The tube was run from a 7-kva. transformer delivering 5000 v. In order to obtain the required densities with manageably long exposures, the current through the tube was reduced to 0.15 amp., representing a current-density in the discharge of about 0.4 amp./cm². Such a current-density is easily obtainable in the small discharge tubes to be found in most spectroscopic laboratories. It was found that the current could be kept constant to within 1 per cent indefinitely.

As spectrograph, the Hilger E2 medium quartz instrument was used with a slit-width of 0.02 mm. The region 2500 to 2000 Å. occupies 9 cm. at the focus of this instrument, and the mean practical resolving-power (purity) is 15,000. On plates measuring 11 × 5 cm., six exposures could be made without using any part of the emulsion within 1 cm. of an edge. It was found necessary to confine exposures in this way to the central regions of the plate for two reasons. Where the processing involved bathing the plate in acetone, the emulsion tended to separate from the glass for several millimetres all round the edge. More important still, in certain of the plates tested, notably the Schumann and Q plates, fogging was nearly always much greater at the edges than in the middle of the plate. Both effects, of course, render accurate comparison of densities near the edges impossible. Another important precaution, whose neglect in the early stages led to trouble, may be mentioned here. The exit aperture of the spectrograph had to be reduced in width to the minimum required, otherwise light scattered inside the instrument during one exposure encroached both on the exposed strip of the previous exposure and on the unexposed strip intended for the next. This would result in a spurious sensitization due to pre-fogging, which could not conveniently be allowed for.

Tab

Plate		Processing	
Name	Sensitizer	Bathed in	Time (sec.)
1. Imperial ordinary	None	—	120
2. Ilford Paget Half-tone*	None	—	120
3. Hilger Schumann	Method 1 (b)	MQ at 20° C.	30
4. Agfa Schumann	"	Process developer ID 13	30
5. Duclaux-Jeantet	Method 1 (c)	Schumann developer	120
6. Ilford Q1†	Method 1 (d)	MQ at 20° C.	120
7. Ilford Q2‡	"	"	120
8. Imperial ordinary†	Commercial kerosene	MQ + 400 per cent excess KBr	120
9. "†	Medicinal paraffin	MQ at 20° C.	120
10. "†	White vaseline	"	120
11. "†	Yellow vaseline	"	120
12. "†	Apiezon M grease	"	120
13. "†	Sodium salicylate	"	120
14. "†	Anthracene	"	120
15. Ilford S.R. panchromatic	"	"	300
16. Eastman ultra-violet	Dihydrocollidine, ethyl carboxylic ester	"	120
17. Agfa ultra-violet§	Unknown	"	120

This plate was originally made as
 * Through the kindness of Dr Bloch
 † Several 11 raids of commercial
 ‡ See footnote, p. 257.

Each of the plates under test was exposed to a constant intensity of radiation for time-intervals of 1, 3, 9, 27, 81 and 243 sec. The plates used and the processing to which they were subjected are listed in table 1. In order to approximate as closely as possible to actual conditions of use, development was confined to the methods recommended by the manufacturers, even though higher densities could be obtained by modifying those recommendations. When possible (as for example when several different sensitizers were used on the same type of emulsion) batches of plates were developed together. Control exposures on ordinary plates were taken at frequent intervals. Subsequent comparisons never revealed visible differences of density between corresponding bands on such plates.

It will be seen that the apparatus required for this method of sensitometry need not be complicated: a low-power transformer operating a simple discharge tube with a slow air-leak provides the source, and a small quartz spectrograph might well be used for taking the photographs. Comparison spectrograms are obtained quite quickly, and the result of most interest can be seen by direct inspection of the finished plates. Thus although we have tested only a few of the plates available for this region of the spectrum, it should be possible for anyone interested in other emulsions to set up the necessary apparatus and have qualitative results within a few hours. Once the records have been obtained, of course, quantitative results can be derived from them, if desired, by suitable photometric methods.

§ 4. DISCUSSION OF RESULTS

It is important to realize that many of the terms used to specify the properties of an emulsion for photography in the visible and near ultra-violet regions are of little significance in the region 2500 to 2000 Å. Since, in general, the $\{D, \log E\}$ curves for an emulsion at these wave-lengths have no straight portions of any considerable length⁽¹¹⁾, such terms as "inertia", "contrast", and "speed" must be considered as having their conventional meanings only in a very general sense. There is no reason, however, why these terms should not be used if they are redefined, not in terms of characteristic curves, but in accordance with their practical significance to the spectroscopist.

In most cases, especially where the source is weak, the spectroscopist wishes first (a) to obtain a measurable record of the spectrum with the least possible exposure, and then (b) to reproduce, as a range of perceptible density-differences, the intensity-differences present in the actual spectrum.

We shall define the *sensitivity* of an emulsion at any wave-length in accordance with (a) above: one plate will be said to be more sensitive than another when the minimum exposure (intensity \times time) necessary to produce a measurable record on the first at the given wave-length is less than the corresponding quantity for the second. Different observers will, no doubt, have different views on what constitutes a measurable record; but these differences will be so small in relation to the actual sensitivity-differences present in the various plates that no confusion is likely to occur. Similarly, the *contrast* of an emulsion at any wave-length will be

defined in accordance with (b) above: one plate will be said to be capable of showing more contrast than another when it will record a greater range of perceptible density-differences between a minimum observable density and saturation.

Our results show that

- (a') no plate tested, except the Ilford Q2 plate, gives more blackening for small values of exposure than does an ordinary plate. That is to say, an ordinary plate is at least as sensitive (according to the definition above) as the sensitized plates, with this one exception. Usually it is more sensitive.
- (b') the sensitized plates, on the other hand, are capable of showing more intensity-contrast than ordinary plates, that is they have a bigger saturation density. This increased density, however, is obtained only by prolonging exposure beyond that which is needed to reach saturation with ordinary plates.

The conclusion (a') above is contrary to the generally accepted ideas on the performance of plates of the Schumann type and sensitized plates in this region. In table 2 are given the numerical results which justify it. They are arranged in the way which, it is hoped, will prove most useful to the spectroscopist who wants to select the emulsion that will record radiation of a given wave-length in the shortest possible time. The numbers given in the table, wave-length by wave-

Table 2. *Minimum exposure times needed to produce measurable records on various plates at different wave-lengths*

Plate*	Wave-length (Å.)	2500	2400	2300	2200	2100	2000
1. Imperial ordinary		1	1	1	1	1	1
2. Paget $\frac{1}{2}$ -tone		7	6	5	5	3	2
3. Hilger Schumann		9	9	4	3	2	1.5
4. Agfa Schumann		9	3	2	1.5	1.3	1
5. Duclaux-Jeantet		3	2	1.5	1	1	1
6. Q1		18	15	12	9	9	6
7. Q2		1	0.7	0.5	0.3	0.2	0.1
8. Ordinary + kerosene		1	1.5	3	3	2	1
9. Ordinary + paraffin		9	14	9	7	4	3
10. Ordinary + white vaseline		2	1.5	2	2.5	1.5	2
11. Ordinary + yellow vaseline		3	2	2	2	2	2
12. Ordinary + apiezon M		9	24	24	15	6	3
13. Ordinary + sodium salicylate		2	2	2	2	2	2
14. Ordinary + anthracene		3	4	3	3	3	3
15. Panchromatic + anthracene		7	5	7	9	27	> 27
16. Eastman ultra-violet		3	2	3	4	3	3
17. Agfa ultra-violet		2	2	3	4	6	6

* For a full description of the plates used and the processing to which they were subjected, see table 1. The numeration is the same in both tables.

length, against a given plate represent minimum exposure times needed to produce measurable records on that plate. The figures at each wave-length are in all cases relative to an ordinary plate as 1, the irrelevant intensity-differences in the nitric oxide spectrum being thus eliminated. Each number was obtained by dividing the

minimum exposure time needed for the test plate by that needed for the ordinary plate. Interpolation by eye was sometimes necessary, since there is a factor of 3 between the stepped exposures. The numbers given are means obtained from two complete batches of test plates. It will be seen that the only emulsion giving numbers less than 1 is the Ilford Q2, though some of the other plates are as good as ordinary plates at some wave-lengths.

These results can also be seen from plates 1 and 2, which will also serve to illustrate our conclusion (*b'*) above. The plates reproduce the 6-step logarithmic exposures made as described earlier on (1) an Imperial ordinary plate, (2) an Imperial ordinary plate sensitized with kerosene, (3) a Hilger Schumann plate, and (4) an Ilford Q2 plate. This selection is fairly representative of the plates tested.

Confining our attention first to one particular band-head, say that at $\lambda 2370$, we find that in the 1-sec. exposures it appears with about equal intensities on the ordinary and the Q2 plates; it is less prominent on the oiled plate and almost invisible on the Schumann plate. The $\lambda 2270$ band appears in 1 sec. on the Q2 plate only. In 3 sec. it appears on the ordinary also, but not until the 9-sec. strip is reached does the oiled or Schumann plate show it. The minimum exposure needed to record the $\lambda 2160$ band is 3 sec. for the Q2, 9 sec. for the ordinary, and 27 sec. each for the oiled and the Schumann plates. For the detection of a weak spectrum, then, the Q2 is as good as an ordinary plate at $\lambda 2500$ and becomes increasingly better towards $\lambda 2000$. The oiled and Schumann plates—and these are representative of all the others—never reach the same sensitivity as the ordinary, though they tend towards it at the shorter wave-lengths.

On the other hand, if we now consider the way in which the density of a given band increases with exposure time, the other effect, (*b'*) above, of the so-called sensitization becomes apparent. The $\lambda 2370$ band, for example, increases its density steadily with time, but not so rapidly on the ordinary plate as on the others. Although on the Schumann plate it is weaker at the start it rapidly strengthens until in the 27-sec. exposure the blackening at the head is greater than on the ordinary plate. Nevertheless farther along the band, where the lines are intrinsically weak, the ordinary plate still holds the advantage. It is this which makes the bands on the ordinary plate appear long and of relatively uniform intensity, whilst on the Schumann plate they seem to be shorter and to comprise lines of a greater range of intensity. Further in the ultra-violet the effect is much more pronounced. On the ordinary plate the $\lambda 2160$ band-head has reached a density which, though low, is nevertheless a maximum, in 27 sec. The oiled plate does not even show the band till exposed for 27 sec., but then it goes on, as the exposure time increases, to densities which no amount of over-exposing would produce on an ordinary plate. If the spectrum to be photographed has intensity to spare, and a negative with strong contrast is required, the oiled plate, the Schumann plate, the Q plates, in fact all the "specially sensitive ultra-violet plates", will give high densities when exposed long enough.

The apparently anomalous results mentioned at the beginning of the paper can

now be explained. A plate is commonly said to be under-exposed when the density is small, or the negative looks thin. This view of the matter, inherited from experience in the visible and near ultra-violet, leads to inflated ideals and correspondingly disappointing results in the region 2500 to 2000 Å. A more useful criterion would be that a plate is over-exposed when the range of intensities of interest is carried over the shoulder of the $\{D, \log E\}$ curve to the nearly horizontal portion. This maximum density for an ordinary emulsion at $\lambda 2300$, say, is so quickly reached that there is a tendency to over-expose enormously in a vain attempt to raise it. Meanwhile, of course, visible and near-ultra-violet radiation scattered in the spectrograph proceed to fog the plate. In addition—and this is more serious—increasing the exposure time brings up the density of the weaker part of the spectrum to that of the stronger, and therefore destroys what little contrast there is. In absorption, for example, weak bands may be entirely lost owing to this effect, whilst in emission, bands of very different intrinsic intensity may appear of equal and uniform strength throughout. While this contrast can be restored by oiling the plate and giving the same exposure as before, it can also be restored in a measure simply by exposing less. Better still, a Q2 plate can be used and a much greater latitude can be obtained without loss either of sensitivity or of maximum density.

Much of the previous sensitometry in this region has been done with sources giving line spectra. The tendency here is to over-expose excessively at the centres of the lines. Under these conditions, the increase of maximum attainable density produced by oiling a plate appears as a spurious increase of sensitivity. No doubt the oiled plate will, as the saying is, “go down further” than the untreated one: certain lines in the far ultra-violet will be strengthened by the process. But a careful examination will show that others, weaker but still visible on the ordinary plate, are removed entirely by oiling. This effect may, of course, be a desirable result in some circumstances. An arc spectrum photographed on Q1 plates, for instance, appears beautifully clean, with fine lines standing out well from a clear background. Nevertheless, the background is clear only because weak lines which would have appeared on an ordinary plate do not appear on the Q1 plate. It is often remarked, for example, that the nitric-oxide bands, which appear in spectrograms of the copper arc on ordinary plates, are not so commonly noticed on similar spectrograms on Schumann plates.

If we leave aside for the moment the Q2 emulsion, the conclusions to be drawn are these. If the intensity of the spectrum to be recorded is low, then oiling is worse than useless, in the sense that it will increase exposure time: the photograph should be taken on an untreated ordinary plate. The price paid will be poor contrast, resulting from a low saturation density. If, on the other hand, the intensity of the source is higher, and the intensity-distribution in its spectrum is of interest, then densities and therefore contrast-values unobtainable on an untreated ordinary plate can be obtained by what is called “sensitizing” it, or by using plates of the Schumann type. The price here will be either the loss of the weaker parts of the spectrum or the necessity for longer exposures. If a Q2 plate is used, however, neither short exposure time nor, within limits, final density need be sacrificed. The price here,

however, is that the spectrogram is apt to appear veiled, and that the mechanical properties of the emulsion film are poor, handling being almost as deleterious to a Q2 plate as to a Schumann plate.

In conclusion, it might perhaps not be out of place to emphasize that the authors do not find, as has sometimes been implied, that ultra-violet sensitive plates are of no use in the region 2500 to 2000 Å., nor that ordinary plates are just as effective for all purposes. It has been shown that it cannot be assumed that oiling an ordinary plate will automatically improve its performance: in many cases quite the opposite will be achieved. Nor is it true that a plate of the Schumann type is always more sensitive than an ordinary plate: frequently it requires longer exposures to reach a given density. Each problem must be considered on its merits, the advantages and disadvantages of each type of emulsion must be weighed, and a plate must be chosen whose performance most nearly fulfils the requirements.

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MONOCHROMATORS FOR PURPOSES OF IRRADIATION

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ABSTRACT. The conditions for a large output of energy by monochromators are analysed and expressed in a convenient form. Description is given of a new type of monochromator for large output, which may be single or double, with glass or quartz optical work. An instrument constant is proposed as a measure of the output-capacity of monochromators.

§ 1. INTRODUCTION

MONOCHROMATORS, in their function of providing approximately homogeneous light from a given heterogeneous radiation, are often desired to possess the to some extent incompatible attributes of high output-capacity and high purifying-power. As these two properties are frequently in conflict, cases arise in which the emphasis falls on the one or the other and we here are more particularly concerned with the case in which major importance is attached to output, while purity and the suitability of the instrument in other respects are required to fulfil subsidiary conditions imposed by the particular purpose in view. Monochromators adapted to such conditions may be single or double monochromators. They are largely employed for purposes of irradiation, for instance of substances under investigation for photochemical or biological change, and are here termed *irradiation monochromators*.

The capacity of a monochromator to receive and deliver high radiation energy depends upon several contributory factors as may be seen from a brief analysis of this property. Let the slit of the instrument be illuminated from a source of radiation having a continuous spectrum, and the illumination on the slit be $(\delta E)_\lambda$ watts per mm^2 per steradian for the wave-length interval λ to $(\lambda + \delta\lambda)$ under consideration. Consider the light-flux Φ passing an element of area of the slit, of height δy and width δx (assumed great enough to prevent diffraction effects) and admitted to the dispersing system by the collimating lens. The distance of the lens from the slit is f_1 and an area A of it is utilized. Then the flux Φ will be given by

$$\delta\Phi = (\delta E)_\lambda \frac{A}{f_1^2} \delta x \delta y.$$

$$\delta x \text{ is determined by } \delta x = f_1 \frac{dI_0}{d\lambda} \delta\lambda,$$

where, assuming the passage of light in the prism system reversed, I_0 is the angle

of refraction on emergence from the system for the direction of the collimator axis.

If then T_λ be the transmission factor of the system for wave-length λ , the corresponding flux $\delta\Phi'$ finally delivered at the exit slit can be expressed in the form

$$\delta\Phi' = P_\lambda (\delta E)_\lambda,$$

where

$$P_\lambda = T_\lambda A \frac{\delta y}{f_1} \frac{dI_0}{d\lambda} \delta\lambda.$$

The quantity P_λ , since it determines what part of the given energy-distribution at the slit is capable of being utilized, represents what may be termed the output capacity of the monochromator for wave-length λ , as distinguished from the inherent character of the incident illumination represented by $(\delta E)_\lambda$ and the selective effect of adjustment of the exit slit. It bears a direct and obvious relation to the Smith-Helmholtz constant for the instrument. The capacity of the monochromator

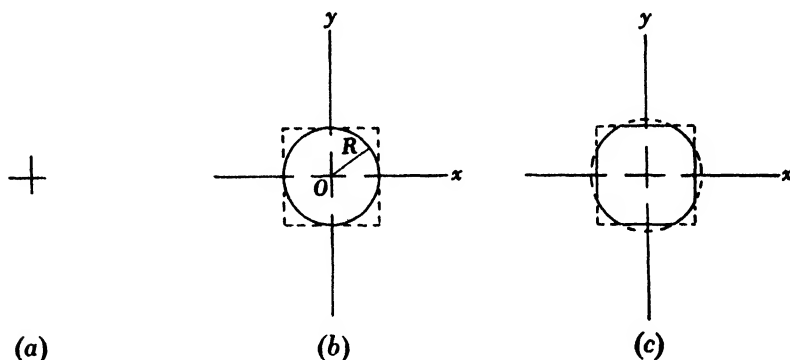


Figure 1.

to receive and deliver radiant energy is thus shown to be proportional to the area of the aperture, the angular subtense of the slit-length at the collimating lens, and the angular dispersion, in addition to the obvious transmission factor T . This factor corrects for losses due to reflection and absorption in the whole system, of which in these respects the prism system accounts for considerably the major part.

As we may assume that the lenses are of small curvature, their approximate contribution to factor T is very simply determined. The usual expression for prismatic transmission does not, however, when dispersion takes place and in the presence of absorption, give a satisfactory value for T_λ , except as applying to a particular element of area of the aperture. The aperture of the instrument, out of consideration for transmission and for other reasons, is often limited, as in (c), figure 1, partly by the prism or prisms and partly by the collimator objective. The extreme cases to which (c) is an approximate mean are depicted in (a) and (b) in figure 1, and in the following the transmission for case (c) will for the purpose of an approximation be assumed to be an exact mean of the transmissions for these extreme cases.

Let the x -axis intersect the collimator axis and lie in the plane of a principal section of the prism system and let the radius OR of the (circular) collimator aperture with centre O be r and let the angle xOR be θ .

Let us further define as follows for wave-length λ the relevant quantities dependent on wave-length. Let L stand for $d\Phi_\lambda/d\sigma$, the superficial density of the flux Φ_λ for a wave-length interval, $\delta\lambda$, in the region of wave-length λ , and per unit cross-sectional area σ in the beam emerging from the collimator; let F be the total transmission factor obtained with Fresnel's formulae, and applied to correct the reflection losses for the whole dispersing prism system; let τ be the fractional transmission per unit length for the material of the dispersing prisms; and let l , a function of x , be the linear light path through the prisms system.

Then for cases (a) and (b) respectively,

$$l = ax + b = ar \cos \theta + b,$$

where a and b are easily determined constants and the zero of θ is chosen so that a is positive. If x_+ and x_- are the limiting positive and negative values of x respectively, and the limiting values of y for case (a) are $\pm Y$, the flux incident on the prism system will be for cases (a) and (b):

$$\Phi_a = 2Y(x_+ - x_-)L,$$

$$\Phi_b = \pi r^2 L.$$

The flux Φ' finally transmitted will be

$$\Phi_a' = 2YL F \tau^b \int_{x_-}^{x_+} \tau^{ax} dx,$$

$$\Phi_b' = 2r^2 L F \tau^b \int_0^\pi \tau^{ar \cos \theta} \sin^2 \theta d\theta.$$

By introducing the variable z , such that

$$z = \frac{1}{2}a(x_+ - x_-) \log_e \tau = ar \log_e \tau,$$

where, be it noted, the natural-logarithmic extinction coefficient $\log_e \tau$ is employed for convenience instead of the usually recorded decadic extinction coefficient, and by dividing by the corresponding value of Φ and integrating, the transmission factor T is obtained for the two cases in the convenient forms;

$$T_a = \frac{\sinh z}{z} \tau^b F,$$

$$T_b = \frac{2I_1(z)}{z} \tau^b F.$$

I_1 here denotes the modified Bessel function of the first kind and first order.

For the mean case (c) the transmission factor T_c will then be given by

$$T_c = \left(\frac{\sinh z}{2z} + \frac{I_1(z)}{z} \right) \tau^b F.$$

As the constant b is the mean path-length when $x=0$, and the expression within the bracket is always in excess of unity, the relative transmission for full aperture

is always greater than the transmission for the mean path-length b . When the absorption is negligible the absorption factors reduce, of course, to unity and the factor T becomes equivalent to F . This completes the analysis of the output capacity of the instrument. The resulting conditions for a high P factor have been studied in the instruments introduced as irradiation monochromators and described in the following section.

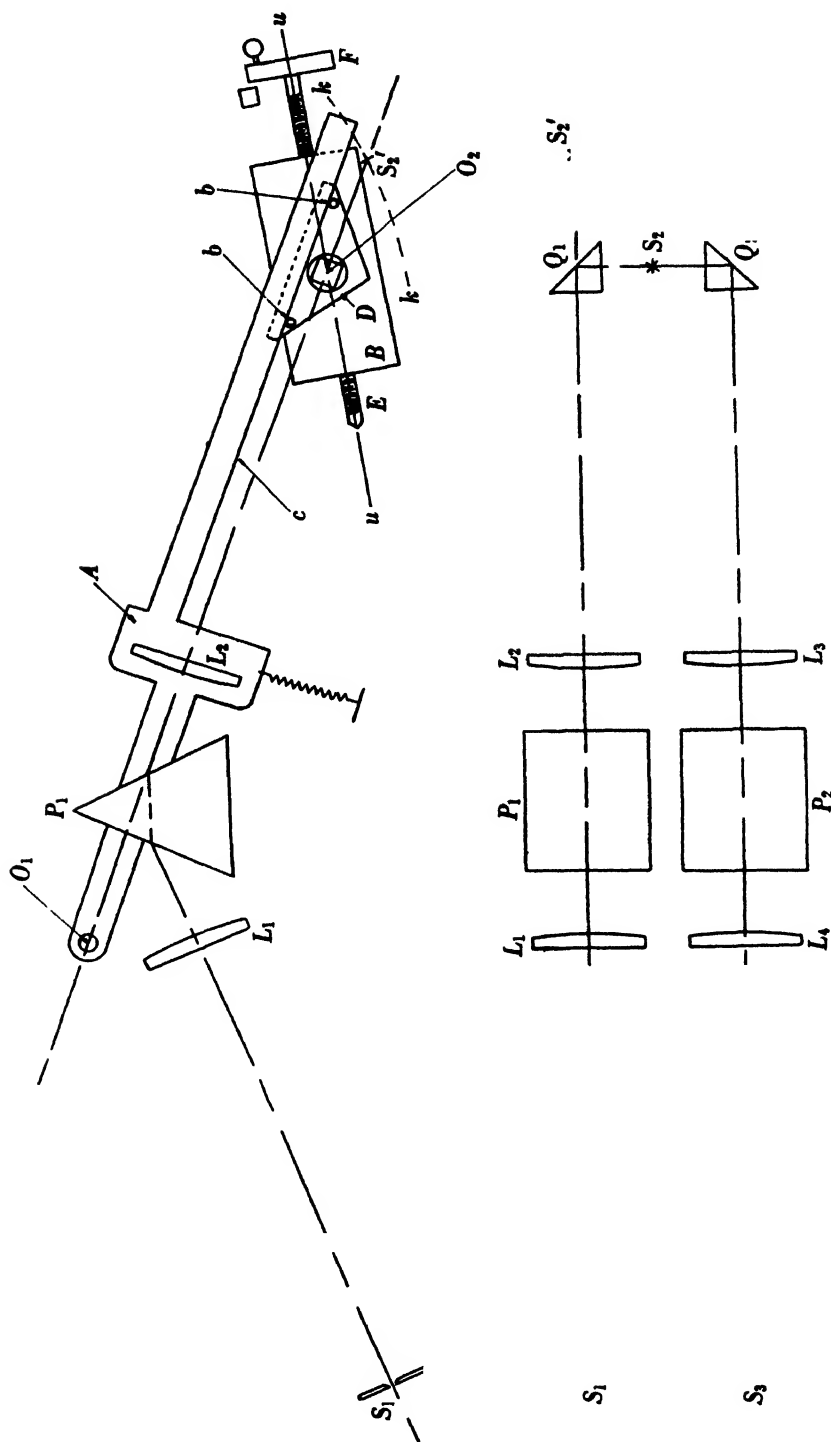
§ 2. DESCRIPTION OF INSTRUMENTS

The novel features of the irradiation monochromators of Messrs Adam Hilger, Ltd., designed by the writer, will now be described. The instruments may take the form of single or double monochromators, and may have optical work of glass or quartz. In each case continuous adjustment of the wave-length with constant focusing is effected throughout the available range by single-hand adjustment of a rotating divided drum and screw.

The double monochromator is constructed in two tiers as shown in the lower half of figure 2. When the instrument is used as a single monochromator, the light in the upper tier proceeds to a slit at S_2' instead of being reflected downwards to slit S_2 by prism Q_1 . L_1 and L_2 are respectively the entrance and exit lenses of the upper half of the instrument, each being single aspherical lenses corrected for the immediate neighbourhood of their optical axes. L_1 is fixed in definite relation to the slit S_1 , while L_2 is mounted on a platform A which may rotate about the centre O_1 but is constrained by rollers bb , which are mounted on a table D rotating about centre O_2 . The straight edge c , rigidly connected with platform A , makes permanent contact against the rollers bb . This straight edge is parallel to a line joining the centres O_1 and O_2 . The centre O_2 is defined by a carefully ground circular fitting in a carriage B , the position of which along a straight slide in the direction uu is controlled by the drum F and screw E , whole revolutions of the drum being indicated by a counter.

Light entering by the slit S_1 traverses the lens L_1 and the prism P_1 , which is fixed, and falling on L_2 is imaged in the form of a spectrum in the focal curve kk . When, for the single monochromator, prism Q_1 is absent, its place is taken by a plane parallel compensating block. Slit S_2' , which is at a fixed distance from centre O_2 and is mounted on the rotating platform D , lies in the focal curve kk and thus selects a certain wave-length band for subsequent utilization. By rotation of the drum F , the position of (i) the lens L_2 , (ii) the carriage along the slide, and (iii) the slit S_2' in its rotation about O_1 and O_2 , may be readjusted for different wave-length settings, while constant focusing is retained at the slit S_2' , as will be seen below.

In the double monochromator, the slit S_2' is absent and the light, reflected into the corresponding slit S_2 by the prism Q_1 , is received again by the prism Q_2 and is delivered to the lower half of the instrument, of which the optical work is geometrically similar to that in the upper half. The lens L_3 is attached to the same platform D as lens L_2 , and the prism P_2 and lens L_4 occupy positions at the lower level corresponding to their counterparts in the upper. The slit S_3 thus selects, after a



ire 2. Diagrammatic view of double monochromator.

further stage of purification, light of the same wave-length as that for which slit S_2 is set.

Under normal circumstances, owing to the need for reducing the number of lenses and consequent loss of light to a minimum, an objectionably curved image inevitably results, but as the lenses L_2 and L_3 rotate about some particular point O_1 , the locus of the conjugate focus at S_2 or S_2' and its departure from a plane are not subject to the restrictions imposed by the laws of static systems, and it has in fact been found possible to correct such focusing errors entirely for three points in the spectrum range by suitable geometrical design, the residual errors at other points within the range being then negligible. This principle* renders the rotating lens adjustment, and the obvious device of superimposing two such mechanisms, capable of providing the basis for an efficient instrument for the present purpose.

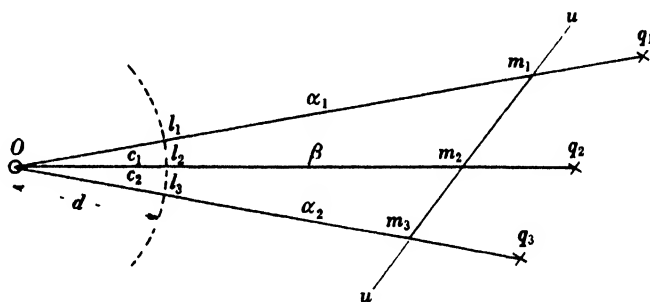


Figure 3.

Reference to figure 3 will explain this. In this figure, O represents the fixed centre designated above as O_1 . The construction has further, in relation to figure 1, the following signification: l_1, l_2, l_3 are points in the locus of lens L_2 at constant distance d from O ; m_1, m_2, m_3 are points corresponding respectively to l_1, l_2, l_3 in the locus of O_2 ; q_1, q_2, q_3 are similarly corresponding points in the locus of S_2' ; C_1 and C_2 are the angles q_1Oq_2 and q_2Oq_3 respectively.

It will be clear from the above, and by reference to figure 2, that if the slit S_2' is at a constant optical distance from the centre O_2 , the variations of the radial distance of O_2 from O_1 must, in order that compensation of variations of the focal distance may be obtained, be equal to these variations. Let the said constant distance O_2S_2' , equal in general to the segment mq in figure 3, be denoted by e , and let the distance from the lens L_2 to focus S_2' be as follows:

$$l_1q_1 = \alpha_1 + e,$$

$$l_2q_2 = \beta + e,$$

$$l_3q_3 = \alpha_2 + e.$$

Then the radii vectors Om_1, Om_2, Om_3 will be $(\alpha_1 + d)$, $(\beta + d)$ and $(\alpha_2 + d)$ respectively. The condition that the locus uu may be rectilinear is then equivalent to the stipulation that the angle $m_1m_2q_2$ as calculated from triangles Om_1m_2 and Om_2m_3

* Patented by Adam Hilger, Ltd.; a British patent specification 374429.

shall have equal values for these two cases. By simple trigonometry this condition gives

$$\frac{\operatorname{cosec} C_1}{\alpha_1' + d'} + \frac{\operatorname{cosec} C_2}{\alpha_2' + d'} = \frac{\cot C_1 + \cot C_2}{d' + 1},$$

where α_1' , α_2' and d' are written for α_1/β , α_2/β and d/β respectively. With slight rearrangement and some reduction this gives an equation for the determination of d' to secure the required condition as follows:

$$Ad'^2 + Bd' + C = 0,$$

where $A = (\tan \frac{1}{2}C_1 + \tan \frac{1}{2}C_2)$,

$$B = \{(\alpha_1' + \alpha_2')(\tan \frac{1}{2}C_1 + \tan \frac{1}{2}C_2) + (1 - \alpha_1') \operatorname{cosec} C_1 + (1 - \alpha_2') \operatorname{cosec} C_2\},$$

$$C = \{\alpha_1' \alpha_2' (\tan \frac{1}{2}C_1 + \tan \frac{1}{2}C_2) + \alpha_2' (1 - \alpha_1') \operatorname{cosec} C_1 + \alpha_1' (1 - \alpha_2') \operatorname{cosec} C_2\}.$$

Of the values for d' so found only one, having a value appreciably less than unity, is generally suitable for application in the present case, on account of mechanical considerations. Its employment results in sharp focusing being obtained at the slit S_2' at the points q_1 , q_2 and q_3 . The errors of focusing at intermediate points measured axially then follow approximately a cubic relation, being of opposite sign for the segments q_1q_2 and q_2q_3 , and amount at maxima to small quantities of the order of $\pm 4 \times 10^{-4}$ of the focal length of the lens L .

In the calculation of d , if e is not constant, owing for example to the presence of some denser medium with dispersion such as prism Q_1 , corrections in the variations of the focal distance should of course be made for this, and likewise it is possible to adjust d so that instead of the locus for the points m_1 being linear, any required departure from linearity at the points considered may be obtained.

The mechanical design of the instrument has been carefully considered. The instrument is housed in a massive casting and remains in permanent adjustment. The lenses are all of aperture diameter 12.7 cm. and of mean focal length 56 cm. The prisms are 11.7 cm. high and have a face-length of 13.0 cm.

As materials, crystalline quartz, glass, and fused quartz are contemplated, but although large pieces of fused quartz may occasionally be available, the absorption per unit length of such material in the requisite dimensions has for the shorter wave-lengths been found to be greater than that of the usual, smaller, first-quality specimens, and the applications of this material are therefore correspondingly restricted. The glass employed is a light flint glass, so that the farthest possible transmission into the near ultra-violet commensurate with reasonable dispersion may be secured. The lines in the mercury spectrum at $365 \text{ m}\mu$. may in fact be seen with this glass system in train. In order that these materials may be employed in the same basic mechanical construction, and on account of their differing refractive indices, the angles of the prisms P_1 and P_2 differ for the various materials, being 60° for fused quartz, and $54^\circ 17'$ for crystalline quartz and for glass.

The linear carriage-travel measures approximately 236 mm. from wave-length 202 to 795 m μ . for each of the quartz systems, and 78 mm. from wave-length 397 to 795 m μ . for the glass system. Settings can be made accurately by division to 0.01 mm. throughout this range; this corresponds in wave-length to 1 angstrom or less (the approximate wave-length accuracy for all wave-lengths less than about 6000 Å.) throughout the spectrum. Calibration tables are supplied with the instrument to connect drum-reading and wave-length. The local inverse dispersion in m μ ./mm. at the exit slit is given in figure 4 in the form of curves for the various materials when the instrument is used as double monochromator. For

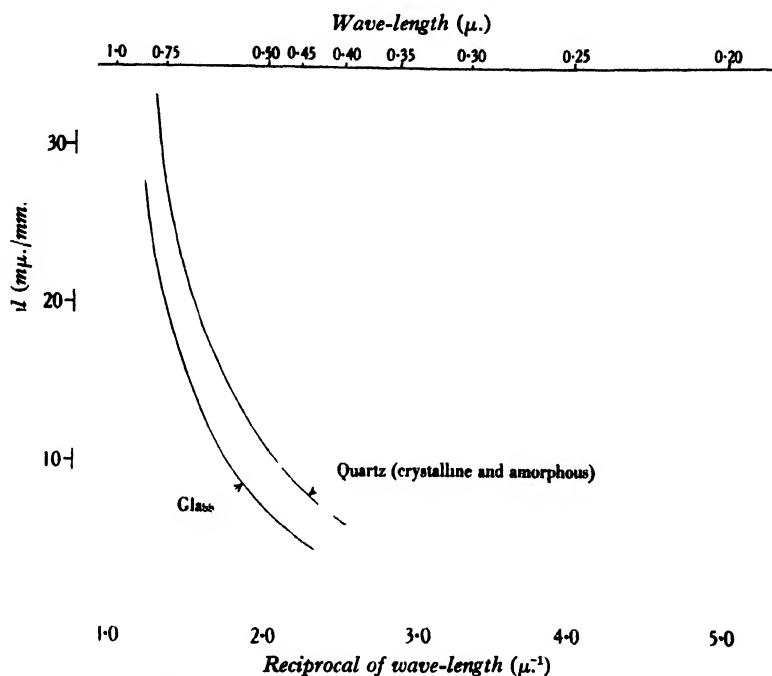


Figure 4. Dispersion reciprocal for double monochromators.

the single monochromators the dispersion-reciprocal would be twice that indicated by the curves.

Provision is also made for converting the instrument into a quartz spectrograph, not by compromise on the optical design of the monochromator but by utilizing the external mechanical construction of the instrument, which lends itself to housing the optical work of a medium-sized spectrograph having lenses of approximately the same focal lengths as those of the monochromator. The optical work of the latter is in fact mounted in such a manner that it may be removed, interchanged for the smaller spectrograph optical work (the collimating and camera lens of which have apertures of 51 mm.), and accurately replaced when desired without need for readjustment. The end cover of the instrument together with the prism Q_1 is removed in this case and a spectrograph camera back takes its place.

APPENDIX

It is the object of the present note to propose, for the property referred to above as output capacity, an approximate and convenient measure which may reasonably be expected to be included in the specification of a monochromator and would be of immediate service to the user of such instruments. As has been indicated in the foregoing sections, the complete expression for the output capacity P_λ for wave-length λ , wave-length interval $\delta\lambda$, and slit-length y , takes the following form:

$$P_\lambda = T_\lambda A \frac{y}{f_1} \frac{dI_0}{d\lambda} \delta\lambda.$$

The implied presence of the absorption factor in the factor T_λ causes an unnecessary complication for the present purposes, owing principally to its variability, but this may be eliminated by considering practically absorptionless regions of the spectrum. The remaining factors are all strictly relevant and form together an easily determined constant for such instruments if definite conventional values be assigned to the variables λ , $\delta\lambda$ and y . Accordingly let λ be $546.1 \text{ m}\mu$. (mercury green radiation), while $\delta\lambda = 1 \text{ m}\mu$. and $\delta y = 1 \text{ mm}$. The output capacity constant, here denoted by P , which is of the dimensions L^2 , then becomes numerically determined by

$$P = T \frac{A}{f_1} \Delta I_0,$$

where the millimetre is the unit of length and ΔI_0 is the angular dispersion of the system for $1 \text{ m}\mu$. at $546.1 \text{ m}\mu$. for reversed passage. In most cases the direction of passage will not appreciably affect the value of ΔI_0 , and a simple calculation, assuming minimum deviation for wave-length $546.1 \text{ m}\mu$., will generally suffice.

It is now proposed that this constant should be stated for all monochromators for which output capacity is of importance, and it is hoped that some agreement may be arrived at on this question among the makers and users of such instruments.

The practical value of this constant may be seen from the following considerations. Given a monochromator of known P and an incandescent source of known emission m ergs per second per mm^2 per steradian per $\text{m}\mu$. at wave-length $546.1 \text{ m}\mu$. in the direction of the collimator axis, imaged by a condensing lens on the monochromator entrance slit, then apart from losses in the condensing lens, the approximate available output at the exit slit is given by simple multiplication roundly as mP ergs per $\text{m}\mu$. per second per mm. of slit-length. By a knowledge of this quantity the suitability of the instrument for various purposes can be directly judged.

The complete expression proposed for P will now be given explicitly in a simplified form, in which we allow for reflecting mirror surfaces and assume the component lenses to be of small curvature and the dispersing prisms to be simple and all of the same angle, all such parts making air contact at each surface.

$$P = \frac{1}{n} \frac{dn}{d\lambda} \frac{Ak \tan I_0}{f_1} T,$$

where

$$T = \frac{1}{2} \left[\prod_{i=1}^k \left\{ \frac{\sin^2 2I}{\sin^2 (I+I')} \right\}_i + \prod_{i=1}^k \left\{ \frac{\sin^2 2I}{\sin^2 (I+I') \cos^2 (I-I')} \right\}_i \right] \left[\prod_{i=1}^j \left\{ \frac{4n}{(n+1)^2} \right\}_i \right] \prod_{i=1}^l R_i.$$

This applies to prisms at minimum deviation and is in a form suitable for logarithmic calculation. In other cases equivalent forms should be used, based on the definition of P .

In this expression λ is the wave-length in $m\mu$, n the refractive index of the denser medium at each refraction, A the utilized area of the collimating lens, and f_1 the distance from the slit to the collimating lens. I, I' are the angles of incidence and refraction respectively at dispersing prism surfaces, and R is the reflection factor at any mirror surfaces included in a given system. The products extend over all the surfaces, respectively k, j and l in number, of (i) the dispersing surfaces obliquely inclined to the incident light, (ii) the dioptric surfaces (lenses and reflecting prisms) normal thereto and (iii) any catoptric surfaces. All instrument-dimensions are in millimetres. The values of the constant P for the instruments above described are as given in the following table.

Material	Single monochromator	Double monochromator
Crystalline quartz	$7.2 \cdot 10^{-4}$	$9.8 \cdot 10^{-4}$
Glass	$14.5 \cdot 10^{-4}$	$18.9 \cdot 10^{-4}$
Fused quartz	$7.6 \cdot 10^{-4}$	$11.3 \cdot 10^{-4}$

ON THE EVALUATION OF SOME HEXAGONAL STRUCTURE FACTORS

BY C. A. BEEVERS AND H. LIPSON, University of Manchester

Received 23 September 1937

ABSTRACT. The formulae $\Sigma \cos h\alpha \cdot \cos (k-i) \beta$, $\Sigma \cos h\alpha \cdot \sin (k-i) \beta$, $\Sigma \sin h\alpha \cdot \cos (k-i) \beta$, $\Sigma \sin h\alpha \cdot \sin (k-i) \beta$, which are very useful in calculating the intensities of X-ray reflection from hexagonal crystals have been tabulated for various values of h and k . In these formulae α and β are the semi-sum and semi-difference of the hexagonal co-ordinates x and y .

§ 1. INTRODUCTION

THE utility of contoured graphs of the structure factors involving only two indices has been pointed out by Bragg⁽¹⁾ and a discussion of the formulae involved⁽²⁾ showed that it is quite practicable to prepare general sets of such graphs, provided too many reflections are not required.

Those of the graphs which contain elements of pattern which are repeated a number of times can be obtained by graphical construction, but in the cases of higher symmetry $P 4b$, $P 4m$, $C 3m$, $H 3m$, $C 6m$, the only available method seems to be to evaluate the function at specific points in the projection and to find the contours by interpolation. Thus one has first to evaluate the figure fields—arrays of numbers giving the value of the structure factor over a network of points. The drawing of the contours from these numbers involves a great deal of further work, particularly if diagrams have to be prepared for reproduction. It occurred to the writers that it would be well worth while to prepare the figure fields themselves for reproduction, and an attempt has been made to gauge the relative values of the two methods of representation.

The purpose of structure-factor charts is two-fold: firstly, an investigator will require the value of the structure factor at any point, and secondly, he will require to know how to move the position of an atom in order to change the value of its contribution in any particular way. For quite general points in the area it is obvious that the contoured graphs are better for both purposes. But if we need consider only those points in the unit cell for which the structure factor has been computed in the preparation of the graphs, it is obviously easier to read off the value from a figure field than to interpolate between two contours. Since, moreover, the contoured graphs would involve a quite considerable loss of accuracy in drawing and reproduction, the authors have been led to prepare sets of figure fields. If required, the contoured graphs can be prepared from these by individual workers, who will then know the accuracy with which the graphs are drawn. The limitation of the

atomic positions to sixtieth parts of the unit cell (as in the tables to be described) is quite immaterial in the early stages of the analysis of a crystal, although further processes may be necessary towards the end of a structure determination.

§ 2. SCOPE OF THE PRESENT WORK

The utility of the structure-factor fields increases with the complexity of the formula, and is therefore most pronounced in the plane groups based on the hexagonal lattice. For the plane groups $C 3m$, $H 3m$, $C 6m$, only three formulae are involved, namely

$$\Sigma \cos h\alpha \cos (k-i) \beta,$$

$$\Sigma \cos h\alpha \sin (k-i) \beta$$

and

$$\Sigma \sin h\alpha \cos (k-i) \beta,$$

where

$$\alpha = \frac{1}{2}(x+y), \quad \beta = \frac{1}{2}(x-y).$$

Although it does not occur in the plane groups the formula

$$\Sigma \sin h\alpha \sin (k-i) \beta$$

has also been evaluated (see § 7), and these computations have been made for the following indices:

$(h \quad k)$						
1 0	1 1					
2 0	2 1	2 2				
3 0	3 1	3 2	3 3			
4 0	4 1	4 2	4 3			
5 0	5 1	5 2				
6 0						

Further, the computation of

$$\Sigma \cos h\alpha \cos (k-i) \beta$$

for orders going up to $h=11$ has also been carried out.* For these high orders, of course, the accuracy for interpolated points is much lower, but nevertheless the charts are exceedingly useful in the determination of structure.

§ 3. METHOD OF COMPUTATION

The evaluation was effected by the aid of the strips prepared by the authors⁽³⁾ for Fourier synthesis, in the following way. Consider the formula

$$\Sigma \cos h\alpha \sin (k-i) \beta,$$

and take the case $h=3$, $k=1$, $i=\bar{4}$. We have to evaluate

$$\cos 3\alpha \sin 5\beta - \cos \alpha \sin 7\beta + \cos 4\alpha \sin 2\beta.$$

For a given value of α this can be evaluated for all values of β by adding three sine strips with amplitude $\cos 3\alpha$, index 5; amplitude $-\cos \alpha$, index 7; amplitude

* By Miss M. A. S. Ross and one of the authors.

$\cos 4\alpha$, index 2. Moreover the values of $\cos 3\alpha$, $-\cos \alpha$, $\cos 4\alpha$ are merely the numbers on the strips $100 C 3$, $\overline{100} C 1$, $100 C 4$, respectively. (Since the strips have been printed only to an amplitude 99, those for amplitude 100 had to be written by hand.) The range of α or β can be extended from the 90° limit of the strips to 180° by reversal of the appropriate strips.

The calculation may also be effected along lines of equal β , the same principles being used. In order to provide an adequate check all the calculations have been done in both ways.

The area covered by the calculations is given by $0 < \alpha < 180^\circ$, $0 < \beta < 90^\circ$. The relation of this area to the unit cell is shown in figure 1 by the singly shaded area. For $C 6m$, the plane group of highest symmetry, this covers three times the area necessary, which is shown doubly shaded in figure 1, but the points outside this area can be brought into it by reflection in the symmetry lines of the plane group, which are the lines in figure 1.

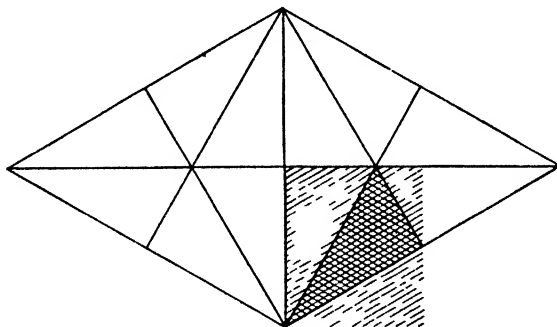


Figure 1. Symmetry lines of the plane group $C 6m$, showing the unique area.

The lines of constant α and constant β after reflection to within the unique area, are shown in figure 2. The intersections of these lines show that a quarter of the points are calculated three times, and the remainder once. This fact affords a very effective check on the general features of the diagram.

In the case of the plane groups $C 3m$ and $H 3m$ the unique area is twice the doubly shaded area of figure 1. The structure factors in these cases, however, have A and B parts, and when the formulae for these parts are considered separately the doubly shaded area of figure 1 proves to be sufficient, as is shown below.

The A part of the structure factors for both $C 3m$ and $H 3m$ is the $\cos.\cos$ formula which has already been dealt with. The B parts are $\cos.\sin$ and $\sin.\cos$. The $\cos.\sin$ formula has lines of symmetry and antisymmetry as shown in figure 3a, and the $\sin.\cos$ formula has these lines as shown in figure 3b. Thus if we are prepared to reflect into the unique area, with a change of sign if necessary, then this area is sufficient for the representation of the formulae.

The planes having h and k divisible by a common factor n were not calculated themselves but were obtained from the appropriate plane of lower order by taking every n th point. Further, the following fact was utilized as a check whenever

possible: If $h-k=3n$, $k-i=3(k+n)$ and $i-h=-3(k+2n)$. Since all these quantities are multiples of 3, the figure field is more highly symmetrical than the

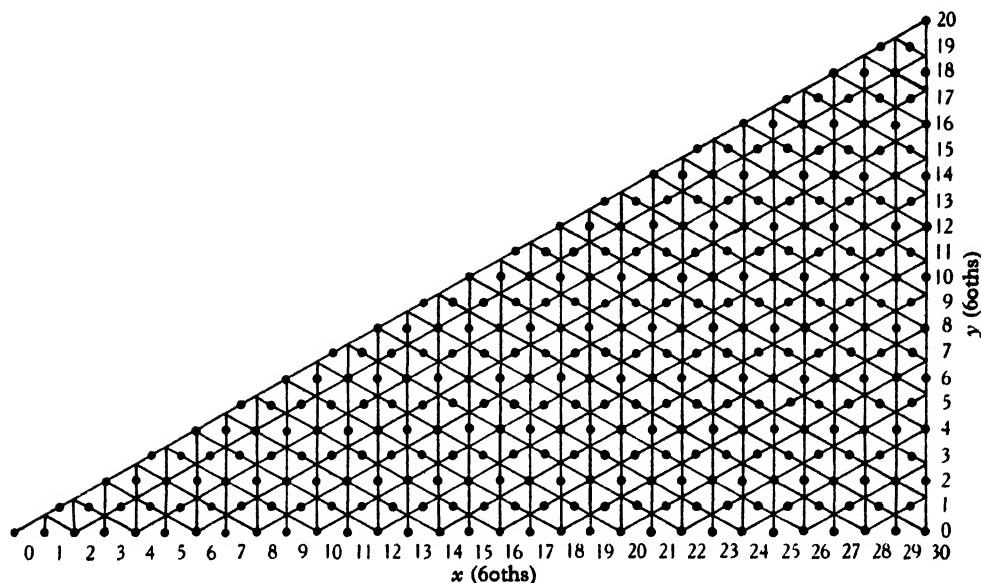


Figure 2a.

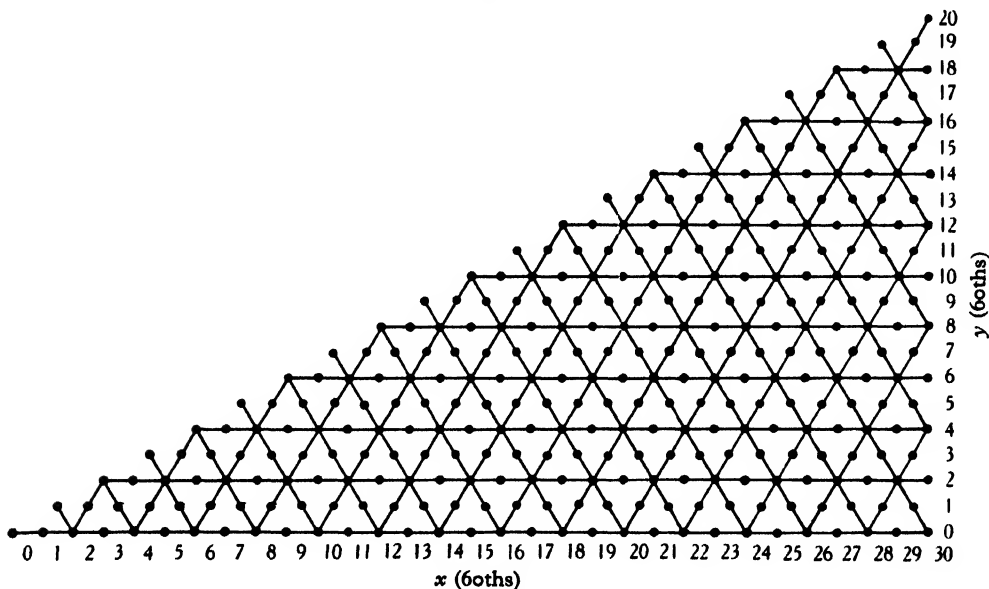


Figure 2b.

Figure 2. Lines of constant α , figure 2a, and constant β , figure 2b, after reflection into the unique area.

general figure field, and it can be derived from the figure field for the plane $(n, k+n, -k-2n)$. For example, the figure field for $(41\bar{5})$ can be derived from $(12\bar{3})$

by interchanging α and β in the latter and then reading off every third line of the field for constant β , and remembering that this changes the formula $\cos.\sin$ into $\sin.\cos$ and vice versa.

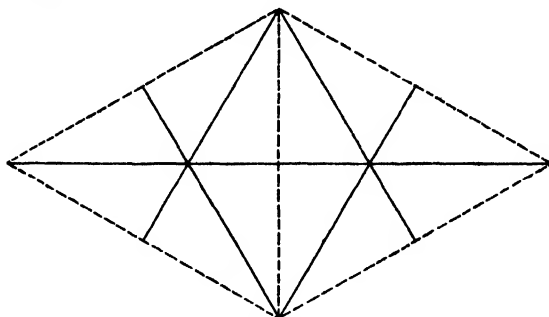


Figure 3a.

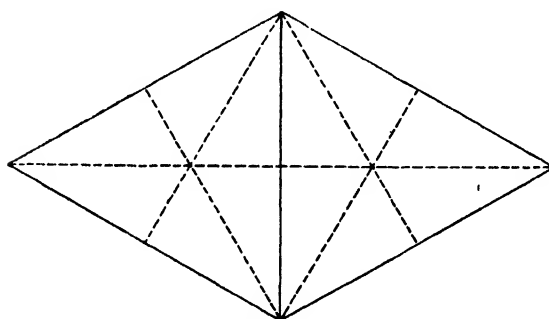


Figure 3b.

Figure 3. Lines of symmetry and antisymmetry (shown as broken lines) in $\Sigma \cos h\alpha.\sin(k-i)\beta$, figure 3a, and in $\Sigma \sin h\alpha.\cos(k-i)\beta$, figure 3b.

§ 4. LIMITS OF INDICES AND PROBABLE ACCURACY

The foregoing process results in the evaluation of the structure factors at intervals of 6° of x and y . This sets a limit to the indices which can be used, for obviously we cannot determine the direction of a shift of co-ordinates if there are not enough points calculated to determine the surface uniquely. The problem is similar to that of resolving-power in Fourier projection.

Owing to rounding-off errors, the final totals are not always correct to one unit, but they are considered to be practically all within $1\frac{1}{2}$ units of the true values.

§ 5. PRACTICAL DETAILS

The figure fields have been reproduced on an Ormig duplicator. The transfers for the duplicating machine were typed in a hexagonal array* covering the unique area. Positive values are in blue and negative ones in red. The co-ordinates in

* Owing to the relation between the vertical and horizontal spacings of the type $\sqrt{3}/2$ used, the angle between the hexagonal axes is actually 121° instead of 120° .

60ths of the unit cell are indicated in green opposite the lines of numbers in the direction of the axes. An example of a field is given in table 1, in which the foregoing colours are represented respectively by Roman figures, Roman figures with lines above, and Italic figures.

If a structure with three or more atoms is being investigated it is probably more convenient to plot the atomic positions to the nearest 60th of the cell-edge on a net which fits the charts and is drawn on transparent paper. The paper can then be laid on the charts and the contributions of the various atoms can be read off.

§ 6. INTERPOLATION

If, for a final calculation of intensities, values of the structure factors are required at finer intervals than 6° in x and y , a process of interpolation can be used. For 3° intervals we want values midway between the points given in the tables. If we assume that the equation to the curve connecting four regularly spaced points having values a, b, c, d is of the third degree, the value at the midpoint of b and c is

$$\frac{1}{16}(-a + 9b + 9c - d).$$

For 2° intervals a formula to give the value at one-third of the distance from b to c would be

$$\frac{1}{81}(-5a + 60b + 30c - 4d),$$

and the value at the centre point of a triangle can be found accurately enough by taking the mean of the values at the corners.

For the highest accuracy, however, the best procedure would probably be to make cross-sections of the field along the various lines and prepare graphically a closer figure field over the area in question. The accuracy with which this can be done is highest for the planes of lower order, but it is believed that an accuracy of about 8 units is possible even in the highest orders of the present tables.

§ 7. APPLICATION TO THREE-DIMENSIONAL STRUCTURE FACTORS

Although the figure fields were originally prepared for use only with $hkio$ intensities, it was found that in some space groups they are of great help in calculating general intensities. They are so when the formula is of the type

$$\sum \cos h\alpha \cos (k-i)\beta \cos lz.$$

In order to make the figure fields more nearly comprehensive, therefore, the function $\sum \sin h\alpha \sin (k-i)\beta$ has also been evaluated, though it does not occur in the plane groups. Moreover, some of the formulae which are not of this type can be expanded in order to allow of the use of the figure fields. For instance the formula for the B part of the space group no. 149, $C 3m1$ can be expressed as

$$\cos lz \cdot \sum \sin h\alpha \cdot \cos (k-i)\beta + \sin lz \cdot \sum \cos h\alpha \cdot \cos (k-i)\beta,$$

which can be computed fairly quickly from tables of $\cos lz$ and $\sin lz$ and the structure factor fields.

§ 8. APPLICATION TO DOUBLE FOURIER SYNTHESIS

The figure fields for the $\Sigma \cos h\alpha \cdot \cos (k-i) \beta$ formula constitute the functions which have to be multiplied by the F of the plane and then added in a process of double Fourier synthesis in a hexagonal crystal. Supposing the process to have been carried out, therefore, the figure fields are exceedingly useful as an indication of the contribution of individual planes to the total synthesis. If the effect of a change of sign of one plane is required, all that has to be done is to add to the synthesis the correct fraction of the figure field.

§ 9. SUPPLY OF COPIES

Workers who would find a set of these tables useful should write to the authors at the University of Manchester, Physical Laboratories. About sixty copies have been made in all, and at the time of sending in this paper twenty-seven sets have already been supplied to various laboratories.

§ 10. ACKNOWLEDGEMENTS

The authors wish to thank Miss Ross (Edinburgh) and Messrs Goldschmidt and Hardy (Manchester) for help in the computations, Miss M. Siddall for help in the typing, and Dr L. J. Comrie for some very helpful advice. One of us (H. L.) was in receipt of a grant from the Department of Scientific and Industrial Research when this work was being done. The authors owe a great debt to Prof. Bragg for his continued interest and encouragement.

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DISSOCIATION ENERGY OF THE CN MOLECULE

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ABSTRACT. The perturbations observed on the vibrational levels of the $B^2\Sigma$ state of CN must be caused by intersections with levels of a $A^2\Pi$ state as established by the widening of the spin doublets of the $B^2\Sigma$ state, i.e. by the simultaneous but unequal shifting of the spin-doublet components and by the decay of the perturbations with decreasing rotational quantum numbers, leaving the rotationless states unaffected. The perturbing state must be identical with the known $A^2\Pi$ state of CN, as proved by the observed positions of the perturbed places in the CN level scheme.

In this way the vibrational set of the $A^2\Pi$ state becomes observable up to the 30th sublevel, where the vibrational convergence is already very marked. A short extrapolation fixes the convergence limit at about $60500 \pm 1000 \text{ cm}^{-1}$ above the ground state $X^2\Sigma$ ($v=0, J=0$) of CN. A comparison of the positions of vibrational levels of the $X^2\Sigma$ and $A^2\Pi$ states shows that the convergence limit of the former should lie in the neighbourhood of the latter; the $B^2\Sigma$ state converges to about $65500 \pm 1000 \text{ cm}^{-1}$.

On this basis the correlation between C+N and CN levels is found as follows:
 $A^2\Pi_{\text{convergence}} \rightarrow C(^3P) + N(^2P) = 60500 \pm 1000 \text{ cm}^{-1}$ and $B^2\Sigma_{\text{convergence}} \rightarrow C(^5S) + N(^4S) = 65500 \pm 1000 \text{ cm}^{-1}$. This could then be verified by the observation of intensity drops at energy values where the other C+N term combinations fall. Thus for the dissociation energy of the CN molecule into tetravalent C(5S) and trivalent N(4S) atoms one gets 8.09 e.v. in very good agreement with calculations made on the basis of $CO(X^1\Sigma) + 11.06 \text{ e.v.} \rightarrow C(^5S) + O(^3P)$.

§ 1. INTRODUCTION

UNTIL recently the dissociation energy of CN could be obtained by calculation only. Usually it was computed on the basis of the dissociation energy of CO in conjunction with thermochemical data, such as the heat of combustion and heat of dissociation of cyanogen (C_2N_2), etc. The chief obstacle to any direct determination in this case lies in the chemical instability of the CN molecule; this is the reason why absorption continua could not be observed and why electron impact methods could not be employed. Even in such cases, however, dissociation limits may often be obtained successfully from perturbation data. The method consists of finding convergence limits of diatomic molecular states by means of perturbations caused by the converging states on other states of the molecule.

The importance of finding the converging set of vibrational states of a molecular term for the purpose of the determination of dissociation limits requires no further argument. Unfortunately the vibrational states which are close enough to each other, and, therefore, to the convergence limit, are often of very high energy; and on account of the Boltzmann factor the probability of transitions to or from them is very seldom high enough to allow their observation as actual electronic

bands. Yet, the closer and higher these states are situated, the more easily may it happen that their sets of rotational levels cross over those of other states having vibrational quantum numbers low enough to give rise to direct observation of bands, in which, under favourable conditions, the courses of those intersections will be observed as perturbations. If the perturbations are numerous and extensive enough, there is always a possibility of deriving the correct positions of the perturbing states from the perturbation data (shifts, doublings, intensity anomalies, etc.). Thus the search for perturbations may be considered as most important in the search for dissociation limits.

§ 2. PERTURBATIONS OF THE CN STATES

Perturbations in the CN bands have been known almost as long as the CN spectrum itself. This spectrum consists of two band systems only, involving three different electronic states. The lowest and highest states are the $x^2\Sigma$ and the $B^2\Sigma$ respectively, the $A^2\Pi$ being situated between them in the energy diagram. It was supposed⁽¹⁾ that the perturbations observed in the violet ($B^2\Sigma \rightarrow x^2\Sigma$) CN bands are caused by the overcrossing of the $x^2\Sigma$ ($v=11$) level by the $A^2\Pi$ ($v=6$) level, and this supposition was afterwards verified⁽²⁾ by observations in the red $A^2\Pi \rightarrow x^2\Sigma$ bands having v equal to 6 for the upper state, where the reverse perturbation could be observed. Although this perturbation has been very well studied, the others, which are numerous and are observed in the bands of the violet system, have not been thoroughly investigated hitherto.

In the $B^2\Sigma \rightarrow x^2\Sigma$ system of CN one distinguishes between the prominent violet bands and tail bands. While rotational analysis and wave-number measurements for the tail bands have been given by Jenkins⁽³⁾, for the former no analysis, in the modern sense, extending to all observed vibrational and rotational states has been published for the prominent bands. This is an obvious lack, as in the search for perturbations the exact knowledge of the precise positions of as many levels as possible is extremely important. While early investigators⁽⁴⁾ of the violet system merely indicated in their wave-length tables the places where perturbations occur, Birge⁽⁵⁾ gave a graph of the perturbations observed in the $2 \rightarrow 2$ violet band, in terms of a numbering, however, which starts from the band head and must be corrected by about 30 units to give the current numbering. However valuable the available data on the violet-band perturbations may be, it was felt necessary to obtain new spectrograms, as the simultaneous inspection of a number of plates greatly increases the probability of detecting all the perturbations. For this purpose a 220-v. d.c. arc was passed between pure carbon electrodes in air and photographed with exposures from 2 min. to 16 hr. in the first and second orders of a 6-m. concave grating (30,000 lines/in.) coated with Hochheim metal on the reflecting surface. This source gives the prominent violet CN bands. To obtain the tail bands, however, the much more complicated excitation with active nitrogen would have been used; by the extreme kindness and courtesy of Prof. F. A. Jenkins, however, we had the privilege of using his own pictures.

While we were trying to systematize the perturbations in the $B\ ^2\Sigma \rightarrow X\ ^2\Sigma$ CN system from a general standpoint, it became more and more apparent that all the perturbations with the exception of two, namely that of the $B\ ^2\Sigma$ ($v=14$) level at the 8th rotational sublevel and that of the $B\ ^2\Sigma$ ($v=15$) level around the 22nd sublevel, could be explained by intersections of the $B\ ^2\Sigma$ vibrational levels with a $^2\Pi$ state. This is proved (i) by the general finding that the perturbations present themselves as widenings of the spin doublets of the $^2\Sigma$ state by unequal shifts of both components of the ρ -type doublets, and (ii) by the observation that also in bands where the overcrossing happens at very low rotational quantum numbers, the doublet width—amounting sometimes to 1–2 wave-number units at the place of crossing—decreases very rapidly to zero with decreasing rotational quantum number, leaving the positions of the rotationless states unaffected (as proved by the entirely regular vibrational scheme of the band system). In theoretical papers on perturbations⁽⁶⁾ it has been shown that the overcrossing of two $^2\Sigma$ states may not affect the doublet width and should cause a shift of the whole set of rotational sublevels, and also of their zero line. The observed kind of perturbation is predicted for intersections of states having $\Delta\Lambda=1$, and since in the case of CN the perturbed one is a $^2\Sigma$ state the perturbing must be a $^2\Pi$.

Once a $^2\Pi$ state is established as the cause of the more prominent perturbations, it seems natural to connect this with the already known $A\ ^2\Pi$ state of CN. How this supposition was indeed verified may be seen in figure 1, which shows the run of the rotational sets of the vibrational levels of $B\ ^2\Sigma$ and $A\ ^2\Pi$ against the abscissa $J(J+1)$. If one makes the entirely acceptable supposition that the coefficient D in the energy term $DJ^2(J+1)^2$ has nearly the same value for all three CN states, the graphs of the rotational energy in that coordinate system could be substituted with sufficient accuracy by straight lines having slopes equal to the numerical values of the rotational constants B_v . For the sake of simplicity, doublet states are represented by their mean value only.

For the $B\ ^2\Sigma$ state the B_v values are obtained from Jenkins's rotational analysis. The places where the $^2\Pi$ -type perturbations occur are marked with circles. The lowest three runs of $B\ ^2\Sigma$ are known up to very high rotational quantum numbers from the spectrum of the arc, which is hot enough for the appearance of band-lines up to $J=100$ and more; in this region the perturbation affects mostly one line only. In the higher vibrational sets of $B\ ^2\Sigma$, however, one often finds more affected lines; we have marked this by doubling the corresponding length of the B runs. This difference in appearance of perturbations at low- and high-lying sets would indeed be expected, because in the crossings by high rotational quantum numbers the two intersecting sets have only very few states with nearly the same energy, while in the crossings with smaller J values the subsequent rotational states remain in the vicinity of each other for more members, and thus the critical interval is much broader. In some bands one finds the unusually wide splitting along the whole length, which shows the rotational set of the perturbing state to run apparently just below the perturbed one, etc. All these features help, of course, to construct the right positions and slopes of the perturbing states.

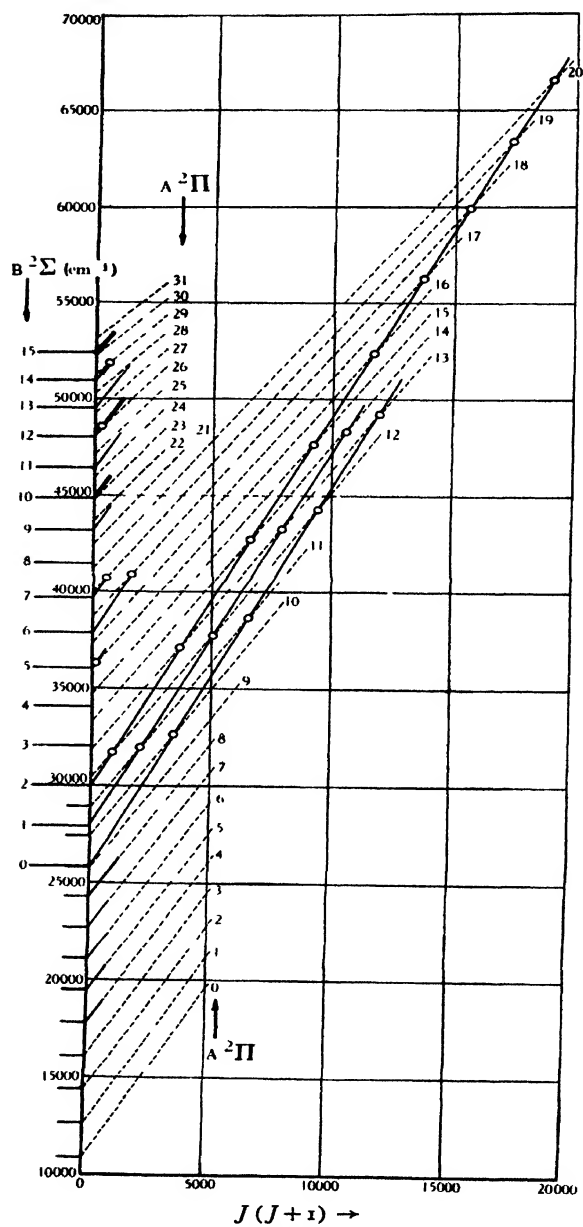


Figure 1.

The deepest-lying $A^2\Pi$ levels in figure 1 have been observed and analysed directly in the CN red bands⁽²⁾. The lengths of the parts observed directly by rotational fine-structure analysis are drawn by full lines. They are of course very short on account of the low effective emission temperature of the source (active nitrogen). The highest three and deepest four vibrational levels of the $A^2\Pi$ state are known only by band-head measurement. It involves only an extrapolation of three steps to arrive right to the position of the first (lowest-lying) perturbation on the $B^2\Sigma$ state, and from there, reasonably decreasing the distances between consecutive vibrational sets and diminishing the slope of the rotational runs, one can go forward from step to step, aided repeatedly by the positions of the perturbations. In advancing up to the 30th vibrational set of the $A^2\Pi$ state one finds the original vibrational frequency and rotational constant considerably decreased—a sign of the closeness of the convergence limit.

§ 3. CONVERGENCE LIMITS FOR THE CN LEVELS

As we advance from $v=0$ up to $v=30$ for the $A^2\Pi$ state, it is found that the decreasing of the distance between two consecutive vibrational states (indicated commonly by ωx in the formula $G(v) = \omega v - \omega x v^2$) must be increased from its original value of 13 cm^{-1} to about 18 cm^{-1} , a very reasonable amount with respect to the length of the vibrational set, for which the $G(v)$ formula should be completed with further terms containing higher exponents of v , of course. As for the position of

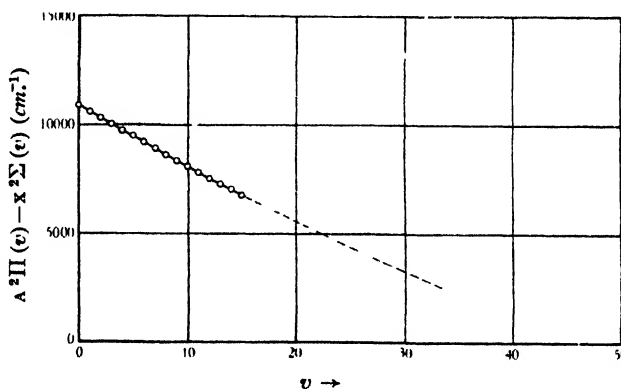


Figure 2.

the convergence limit one has to proceed by further increasing this decrement, and since the law of this process is at present unknown, at first glance one may believe the result to be very arbitrary. However, a checking up shows this not to be the case; it is found that by assuming the $G(v)$ function to be first as cubic, then of fourth, fifth degree, etc. in respect of v , one gets values for the convergence limit within an interval not exceeding at most 1000–1500 wave-number units. An upper limit is given by the progress observed in the last ωx values, which would reach the last ΔG value within about 20 steps, thus fixing $v_{\max} < 50$.

Some kind of control to the convergence of the $G(v)$ values is afforded by the B_v values of the $^2\Pi$ state, as these should show a convergence to zero at just the same v where $G(v)$ reaches its maximum. By trial one finds the most probable position of the Λ $^2\Pi$ convergence limit to be about 60500 cm^{-1} above the CN ground state, with a probable accuracy of $\pm 1000\text{ cm}^{-1}$, and $v_{\max} = 47$.

A comparison of the vibrational sets of the x $^2\Sigma$ and Λ $^2\Pi$ states shows that their convergence limits should lie very near together. This is strongly suggested by figure 2, where the term-differences Λ $^2\Pi(v) - x$ $^2\Sigma(v)$ are drawn as ordinates against the common v 's as abscissae. One finds that the observed differences fall along a nearly straight line, which seems to cut the v -axis just in the region where the v_{\max} for Λ $^2\Pi$ should lie. In a previous paper⁽⁷⁾ insufficient attention was paid to the relative position of the x $^2\Sigma$ and Λ $^2\Pi$ levels; this resulted in the incorrect conclusion that beyond the intersection of the two potential curves, these two states may converge to limits differing in energy more than 0.5 e.v. , an error now corrected. In the same paper, in an effort to get the dissociation products of the CN molecule, the Rydberg extrapolation method was used to obtain the convergence limit of the B $^2\Sigma$ state. Now it turns out that this method yields too low a value. This fact was definitely established by computations on the a' $^3\Sigma$ state of CO, where the positions of about 40 vibrational levels, from the first up to just below the convergence limit, are well known⁽⁸⁾. Fortunately, in the case of the B $^2\Sigma$ state of CN the value of ωx increases within the observable 15 steps from 21 cm^{-1} to about 28 cm^{-1} , thus making the extrapolation rather short and keeping the error between narrow limits. By extrapolation with a $G(v)$ formula containing members up to the third power in v one gets a value for the convergence limit for B $^2\Sigma$ of about 39700 cm^{-1} above the $v=0, J=0$ level of the B $^2\Sigma$ state, in good agreement with the computations based on the slope (i.e. α) of the B_v function, this, too, being large enough for a short extrapolation. In this way the most probable position of the convergence limit of B $^2\Sigma$ comes out to be $65500 \pm 1000\text{ cm}^{-1}$ above the CN ground state, since the position of B $^2\Sigma(v=0, J=0)$ level amounts to 25800 cm^{-1} , i.e. it is the highest of all three CN states, and this corrects the other error in the previous paper⁽⁷⁾.

Figures 3 and 4 show the vibrational energy $G(v)$ and the rotational constant B_v for the three CN molecular states as functions of the vibrational quantum number v . The dotted parts are obtained by the most probable extrapolation mentioned above, and by the requirement that $G(v)$ should arrive at its maximum at just the same v where B_v becomes zero.

§4. CORRELATION OF THE CONVERGENCE LIMITS WITH ATOMIC LEVELS

The conclusion, established entirely experimentally, that the convergence limits of the CN states are as close-lying as about $5000 \pm 1000\text{ cm}^{-1}$, i.e. 0.6 e.v. , may serve as a basis for the determination of the correct correlation with the levels of the separate atoms.

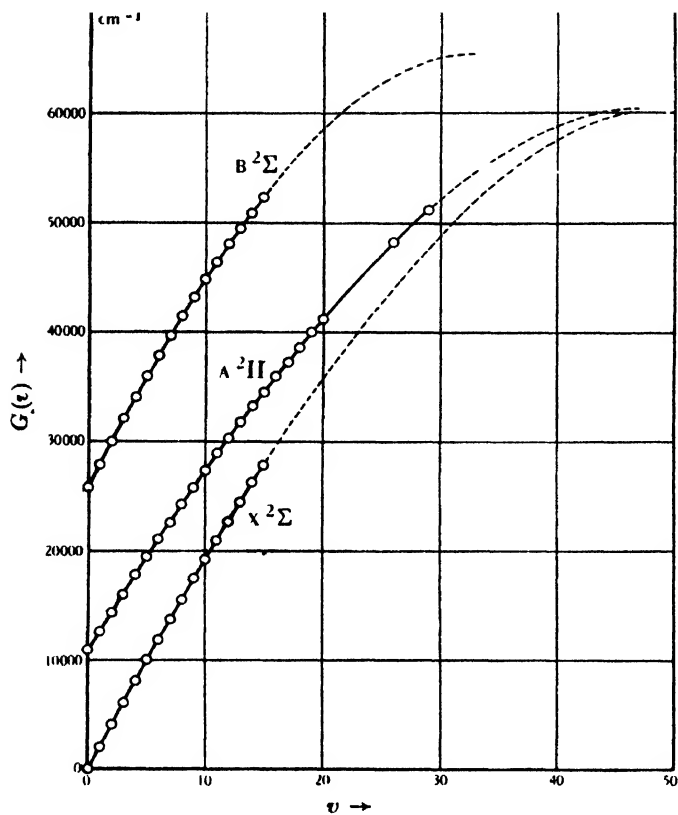


Figure 3.

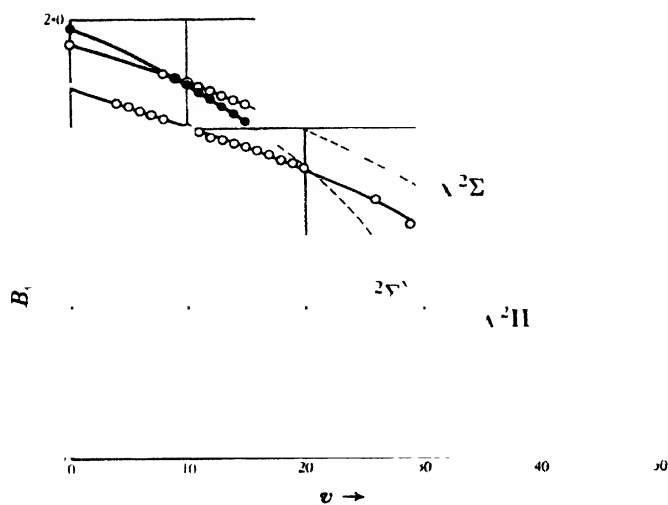


Figure 4.

Since the lower convergence limit belongs to a $^2\Pi$ state in which the doublet width seems to be not much affected within the observable interval from $v=0$ to $v=11$, one may expect that the corresponding atomic term combination will consist of atomic multiplet terms showing multiplet separations of about the same order of magnitude as the $^2\Pi$ state. Indeed, from the whole set of the atomic C and N terms there is only one, namely C (3P), which may fulfil this requirement, its overall width amounting to about 40 cm^{-1} , while the doublet separation of a $^2\Pi$ is about 50 cm^{-1} in the observed set of levels.

If one wishes to find now a pair of C + N combinations, the lower combination having the C as 3P and the upper combination being about $0.6\text{--}0.7\text{ e.v.}$ above the lower, to give rise to a $^2\Sigma$ level, there is only one choice: C (3P) + N (3P) for the lower and, at some 0.63 e.v. higher, C (5S) + N (4S). The distance between the two other possible combinations: C (3P) + N (2D) and C (3P) + N (2P) is about twice as large,

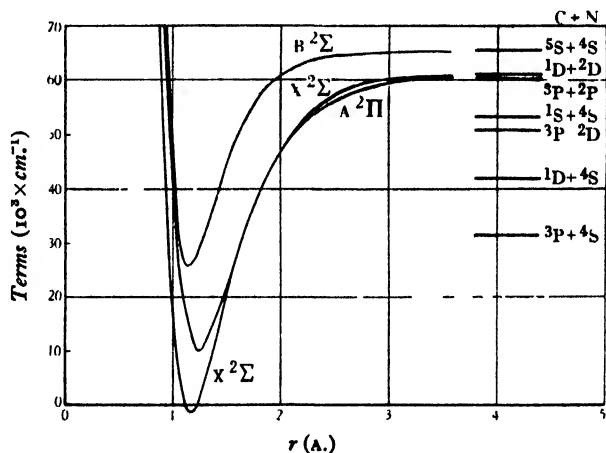


Figure 5.

and thus they may certainly be ruled out. Figure 5 shows the potential energy curves of the three CN states in relation to the C + N levels; the potential function assumed is Morse's with D equal to 60500 cm^{-1} and 39700 cm^{-1} respectively.

Having fixed the atomic term scheme with respect to the molecular ground state, one has to investigate what is taking place at the energy values where the other atomic term combinations occur.

As was mentioned earlier, among the perturbations observed in the vibrational levels of $B\ ^2\Sigma$, there are two (namely those of $v=14$ and $v=15$) which differ in many respects from the others. The latter cases—already recognized as $^2\Pi$ perturbations—show no intensity anomalies at the places of the perturbations. In the two anomalous cases, however, it happens that not only are there intensity anomalies but also the positions of the lines are affected in a different manner, the ρ -type doublet widths sometimes varying in a very rhapsodic way. In seeking reasons for these two anomalous perturbations one may undoubtedly assume that perhaps they are caused by intersections of the sublevels of $B\ ^2\Sigma$ with sublevels of $X\ ^2\Sigma$, for instance.

The low-lying B levels are indeed overcrossed frequently by higher-lying X levels still in the observable region of the violet bands, but there is no sign of any perturbation.

The place of the higher-lying anomalous perturbation is the $v=15$ level of the B $^2\Sigma$ state, in the neighbourhood of the 22nd rotational sublevel, at a height of about 53400 cm^{-1} or 6.6 e.v. above the ground state. While the $R(20)$ line of the $15 \rightarrow 15$ violet band has normal intensity, $R(21)$ is increased abnormally; $R(22)$ is normal again, but $R(23)$ is very weak; $R(24)$, $R(25)$ and $R(26)$ have normal intensity but $R(27)$ is very weak, and beyond these no more lines are observed. Further, while the $15 \rightarrow 15$ band is relatively intense, there is no trace of the $16 \rightarrow 16$ band or of others with $v \geq 16$. All this seems to correlate to the fact that the atomic term combination C (1S) + N (4S) lies just at this height, thus indicating as an interpretation a perturbation in the vicinity of a predissociation limit, such as is observed among others in the CO Third Positive bands⁽⁸⁾.

For the lower-lying anomalous perturbations ($v=14$) the findings in the $14 \rightarrow 14$ violet band are, in short, that the lines $R(8)$, $R(11)$, and $P(10)$, $P(13)$ show anomalous intensities and irregular doublet widths, while the other lines before, between and beyond these seem to be unaffected. This phenomenon takes place in the CN level-scheme at about 51000 cm^{-1} above the ground state, and this suggests as an interpretation an interaction of the $v=14$ level of B $^2\Sigma$ with some other level (or levels) arising from the atomic term combination C (3P) + N (2D), the position of which is at 50900 cm^{-1} .

The next atomic term combination, which has not played a role in this scheme of CN dissociation, is C (1D) + N (4S) at 41900 cm^{-1} . A band of the violet system, having the upper level at this height, would fall however in the crowded spectral region where the heads or the tails occur, and must escape reliable observation.

The lowest combination C (3P) + N (4S) is situated at 31700 cm^{-1} . The two lower states (X $^2\Sigma$ and A $^2\Pi$) of CN have their highest vibrational levels just below this energy value; the B $^2\Sigma$ state has its fourth level ($v=3$) at this height. Now on spectrograms taken with an arc as source one often finds that bands of the violet system with initial vibrational quantum number $v' \geq 3$ do not appear with an intensity comparable to that of bands with $v'=0, 1$ and 2 . For instance on our plates (taken with a d.c. arc in ordinary atmospheric air) one finds the R branches of the B $^2\Sigma \rightarrow X^2\Sigma$ bands, $0 \rightarrow 0$, $1 \rightarrow 1$ and $2 \rightarrow 2$ at high rotational quantum numbers (up to $J=100$ and more) placed in characteristic groups, namely three pairs of lines due to the spin doubling of the $^2\Sigma$ states, always with almost equal intensity, while there is no trace of a $3 \rightarrow 3$ band. In view of the very considerable intensity of the bands with $v'=2$ one would not expect the sudden drop for bands with $v'=3$. Of course by excitation with active nitrogen this does not hold at all. As for interpretation, it seems probable that the levels arising from the combination C (3P) + N (4S) may cause a predissociation at the B $^2\Sigma$ ($v=3$) level. In this case the border line of the predissociation should cut the $v=2$ run at very high quantum numbers only, a case already met in the N₂ spectrum⁽⁹⁾.

§ 5. DISSOCIATION ENERGY OF CN

The correlation of C+N atomic levels to the convergence and predissociation limits of CN fixes the distance of the lowest atomic combination C (3P) + N (4S) in respect to the $x^1\Sigma$ ($v=0, J=0$) ground state of CN at about 31700 cm^{-1} or 3.91 e.v. ; in the usual way this value would be called the energy of dissociation. However, as has been pointed out⁽⁸⁾ in the case of carbon compounds, it seems to be more reasonable to restrict this name to the energy necessary to split the molecule into a tetravalent carbon and a trivalent nitrogen atom: C (5S) + N (4S). This level lies at about 65500 cm^{-1} or 8.09 e.v. , and thus the dissociation energy of CN should be given by this value.

We have arrived at the value of D (CN) in this paper on an entirely experimental basis, and it is interesting to know that it agrees very well with the calculated one. This calculation is based partly on thermochemical cycles fixing the difference of dissociation energies of CO and CN at about 70 kcal. or 3.05 e.v. , and on the value of the dissociation energy of CO itself, which latter should be obtained by spectroscopic (or electron-impact) experiments. As has been shown⁽⁸⁾, the spectroscopic and electron-impact results concerning the dissociation phenomena of CO (and also the corresponding results on CO_2 , which are entirely connected with those on CO) may be interpreted without any contradiction only on the basis of a correlation of C+O levels to the CO states fixing the combination C (5S) + O (3P) in respect to the $x^1\Sigma$ ($v=0, J=0$) ground state of CO at the height of 11.06 e.v. , a value called by us the dissociation energy of CO. Thus the calculated value of D (CN) is equal to $11.06 - 3.05 = 8.01\text{ e.v.}$

In a forthcoming paper it will be shown that all the observed dissociation phenomena in carbonic compounds (electron impact, light absorption, etc.) could be interpreted in the simplest and easiest way, and without any contradiction, by dissociation into C (5S) atoms.

§ 6. ACKNOWLEDGEMENTS

This paper has been completed in the spectroscopic laboratory of the Physical Institute of the Royal Hungarian University for Technical and Economic Sciences, Budapest, directed by Prof. B. Pogány. The authors wish to express their deepest gratitude to the Council for Natural Sciences and the Széchenyi Society for their material aid, and especially to Prof. F. A. Jenkins of the University of California, for his kindness in lending to the authors his precious spectrograms of the CN tail bands.

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NOTE ON THE WHISPERING GALLERY OF ST PAUL'S CATHEDRAL, LONDON

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Received 12 December 1937. Read 28 January 1938

ABSTRACT. The apparent disagreement between Rayleigh's deduction and those of Raman concerning the whispering-gallery phenomenon is shown to depend on the fact that Raman used a sustained source which gave rise to interference, whereas Rayleigh dealt with a whisper projected in one direction. Further, it is shown that, whereas Rayleigh attributed the success with a whisper to the fact that it is composed of high frequencies, low frequencies are projected equally well, and that actually the success attained with a whisper is due to its low intensity, which does not give rise to audible echoes. Explanations are offered of the circumferential and radial alternations of sound mentioned by Raman and Sutherland.

§ 1. INTRODUCTION

SABINE⁽¹⁾ referred to a whispering gallery as one so shaped that faint sounds can be heard at extraordinary distances, as a result either of focusing or of the creeping (as Rayleigh⁽²⁾ termed it) of sound waves round a curved wall. The phenomenon in those buildings in which focusing occurs requires no explanation, and is usually apparent at one region only, the focus; but the galleries of the second category, that in St Paul's being the classic example, still await complete explanation.

The gallery in St Paul's runs round the inside of the dome and overhangs to the extent of some 1.5 m. An iron railing about 1.25 m. in height is on the inner side of the gallery, and the side of the dome forms the outer boundary; a low stone seat runs round the side of the dome. The dome itself is, of course, high above the gallery. A guide, whispering near the wall of the gallery, can be heard easily by a person seated at any point of the circumference. A whisper is more effective than a shout.

Airy⁽³⁾ suggested that the dome overhead acted as a concave reflector, but Rayleigh⁽⁴⁾ pointed out that this explanation is untenable, for in these circumstances the sound, after reflection, would be focused on to the section of the gallery opposite the source, whereas the sound is more or less evenly distributed round the gallery. "The whisper seems to creep round the gallery horizontally, not necessarily along the shorter arc, but rather along that arc towards which the whisperer faces."

§ 2. RECENT OBSERVATIONS

More recently Raman and Sutherland⁽⁵⁾ have detected radial and circumferential variations in the intensity of the sound in the gallery, and state that "The circumferential fluctuations of intensity might be interpreted as being, at least in part, due to the stationary interference of waves which meet after passing in opposite directions round the gallery. But the radial fluctuations are less easily explained, and must be regarded as fundamental in any satisfactory theory of the whispering gallery."⁽⁶⁾

Raman⁽⁷⁾ has since shown that the waves do run round the walls as Rayleigh had suggested. He did this by tapping a point on the circumference, timing ten echoes and deducing the velocity on the assumption that the sound travelled round the walls, the values obtained agreed with that of sound in the open air to within 1 per cent. The experiment was performed in several galleries in India, some of which had not been suspected of possessing whispering-gallery properties until he pointed them out.

The writer, by permission of the authorities of St Paul's Cathedral, was able to carry out some experiments in the whispering gallery after it had been closed to the public. The frequencies used ranged from 256 to 6000 c./sec., the sources of sound being heavy tuning forks capable of vibrating for a considerable time. They were held in turn at different distances from the wall, and in every case the sound was heard by observers close to the wall, but the positions of the radial and circumferential alternations varied with frequency and with the distance of source from the wall. It should be remembered that the maximum distance of the source from the wall was about 1.5 m.

§ 3. EXPLANATION OF THE PHENOMENON

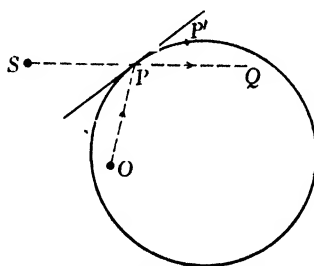
The fact that the low frequencies travelled round the gallery is of particular interest, for a whisper is composed of high-frequency sounds, and to this fact, in part, the phenomenon has been attributed. Actually the success attained with a whisper appears to be due to the fact that the open-air range of whispered sounds is small, and that the sound traversing a diameter would be imperceptible at the side opposite to the source, and would not interfere with the circumferential waves.

The sound which is heard is that which travels round the wall by successive reflections along short chords. This sound suffers very little absorption at the hard smooth wall during reflection, so that the main energy-loss would appear to be due to the divergence of the sound. This, however, is minimized by the reinforcement of incident and reflected waves which combine to produce waves with fronts travelling at right angles to the wall.* At the wall they are in phase, but at a short distance from it (the distance depending on the frequency) they are out of phase, and

* Compare this with the observations of Scott-Russell (B.A. report 1844) on water waves. He found that when the waves were incident on a vertical wall in deep water at an angle of incidence greater than about 75° , the waves were not reflected but passed along the wall, the wave-front being at right angles to the wall.

approximate silence will result. A little farther away from the wall the waves will be in phase again, but with a diminished intensity.

The existence of these waves may be shown by sprinkling the floor of a small model with lycopodium powder and passing a vertical electric spark of suitable intensity near the wall.⁽⁸⁾ (The wave-length of the sound from the spark is probably of the order of one or two centimetres.) The powder is ranged into short ridges at right angles to the wall, which indicates progressive waves near the wall, for if sparks are passed on an open plate, the powder is ranged in continuous circular ridges with the spark as centre; the rings are thus at right angles to the direction of the air-vibration. The distance between the ridges or striae diminishes with intensity.



Plan of gallery. O , source; S , image of O at P ; S' , image of O at P'

The formation of the waves can be explained by the method of images.^(8, 9, 10) Let the circle represent the plan of the gallery; if O be the source of sound and OP a particular ray of sound, the tangent through P represents the plane mirror which reflects OP to PQ , S being the image for the reflected ray which arrives at the point P . The two sources of sound O and S project a narrow beam midway between and at right angles to OS . The actual portion of this beam in the neighbourhood of P is that inside the circle. For an adjacent point P' , the image will be S' ; thus there is a series of moving images each of which combines with the primary source to form waves with the wave-front at right angles to the circumference. This wave-front will be narrow, for the incident and reflected waves will be in phase only at the circumference.

At a small distance from it they will be out of phase, and approximate silence will result. Farther still, i.e. nearer the centre, the waves will be in phase again, and give rise to audible sound, an effect observed by Raman and Sutherland.

For the more remote parts of the circumference the primary and secondary images will be responsible for the propagation. At a particular point the sound may arrive in two different beams moving in the same direction round the gallery but with different path-lengths. Whether these are in phase or not at that point determines the intensity of the sound, and thus arises the circumferential variation in intensity.

§4. THEORY APPLICABLE TO CONTINUOUS SOUNDS

Another theory suggests⁽⁵⁾ that this variation may be caused by interference between the two sets of waves which leave the source and pass round the gallery in opposite directions to meet. This, however, is unlikely in a whispering gallery, for the overlap of different syllables at all points except that opposite the source would make the words indistinguishable. Besides, the whisper seems to creep round the gallery in the direction the speaker faces.⁽²⁾

If the whisper is replaced by a source of sound this theory will hold, and the circumferential variations will be definite, whereas with a whisper they are not. This probably explains the disagreement between Rayleigh and Raman—in fact, the latter states that the circumferential variations are most marked at the side of the gallery opposite to the source.

Raman and Sutherland experimented with a miniature gallery composed of a complete circular reflector with a Galton whistle as source; they found that the circumferential variations were uniformly spaced. When, however, a semicircular reflector was used with the source at one end, the variations were found to be unevenly spaced, being more crowded together near the end of the diameter opposite the source.

§5. CONCLUSIONS

The conditions necessary for the whispering gallery effects are (i) a hard wall for good reflection, (ii) a source of sound of sufficiently low intensity to suffer no appreciable reflection from the opposite side of the gallery, and (iii) a source near the wall and directed so that the angle of incidence is large.

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DISCUSSION

SIR CHARLES V. BOYS. It seems to me that some photographs* which I took in the year 1892 might have some interest. The two to which I particularly refer were taken with a view to obtaining ocular evidence on the effect of a single wave front,

* Reproduced by Larmor, *Memoir and Scientific Correspondence of Sir George Stokes*, Vol. II, pp. 341-343.

(1) when this is so much inclined to a reflecting surface as to give perfect reflection, (2) when it is nearly perpendicular to the reflecting surface, and (3) when the two actions (1) and (2) are merged. There is no question here of the low intensity of a whisper nor of sustained vibrations, but the single wave of compression when nearly perpendicular to the reflecting surfaces converges upon it and swallows all the energy of any reflection, becoming denser and travelling more quickly.

Dr G. SUTHERLAND. Prof. Raman and I never really had an opportunity of being at St Paul's long enough on end to investigate the matter thoroughly, and I am very glad the author has carried the matter further in this way. What does he make of Sabine's contention that the effectiveness of St Paul's is partly due to the fact that the sides are slightly inclined inwards?

AUTHOR'S REPLY. I am much indebted to Sir Charles Boys for lending me the original lantern slide showing the phenomenon he refers to. The fact that a wave front which at first is really normal to the reflecting surface finally becomes normal in the vicinity of that surface agrees with the note at the foot of page 294.

In answer to Dr Sutherland: if a beam of sound is initially horizontal and strikes a sloping surface in which the normal at the point of incidence is depressed, the beam will be reflected downwards. In St Paul's the concave inclination is very slight, and has the effect of keeping the sound in the gallery. The floor, of course, assists this.

THE VARIATION OF VOLTAGE-DISTRIBUTION AND OF ELECTRON TRANSIT TIME IN THE SPACE-CHARGE-LIMITED PLANAR DIODE

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ABSTRACT. In an earlier paper the solutions for the voltage-distribution and electron transit time in a planar diode were restricted to the case of temperature limitation. In this present paper the case of space-charge limitation is dealt with. Langmuir's equations for the voltage-distribution are put into a more convenient form, and expressions are then derived to show the dependence on emission current of the interelectrode current, the cathode field, and the electron transit time for any normal values of emission velocities.

§ 1. INTRODUCTION

IN recent years considerable attention has been paid to the conditions existing in the interelectrode spaces of the thermionic valve, and several papers have been published in which the behaviour of simplified models under the action of alternating voltages has been treated mathematically^(1, 2, 3, 4). They have all shown the importance of the electron transit time in determining the behaviour of a valve when alternating voltages are applied. When, as is usual, these voltages are small, the transit time differs only slightly from its value under static conditions, and this can therefore be used as a close approximation.

In an earlier paper⁽⁵⁾ the author has examined mathematically the variation of static transit time in the temperature-limited plane diode. The general solution for the voltage-distribution was derived from the differential equation of motion, and the effect of initial velocities was treated by assuming that all the electrons were emitted with the same velocity u_0 , given by

$$u_0 = \left(\frac{\pi k \theta}{2m} \right)^{\frac{1}{2}}$$

instead of being emitted with the Maxwell distribution. This approximation was shown to be valid as long as the diode remained temperature-limited, that is, for all currents from zero up to that value which just reduced the cathode field to zero. Within these limits it was possible to express in convenient form the variation with current of the voltage-distribution, the cathode field, and the electron transit time, for any normal value of initial velocity. The variation of transit time within these limits is of importance in explaining the cause of electron oscillations⁽⁶⁾; and a knowledge of the variation of the cathode field will be necessary in any examination of the upper bend of the {current, voltage} characteristic of the diode, and in the correct interpretation of the Schottky⁽⁷⁾ effect in this region.

It is more usual however for a valve to be working in a condition of space-charge limitation. It will be convenient to define at this point the terms to be used in describing the interelectrode conditions in the diode. With a fixed anode voltage V_a the voltage-distribution is determined mainly by the emission current i_e . Thus the diode is *temperature-limited* for any value of interelectrode current i up to the saturation value i_0 which just reduces the cathode field to zero; in this condition the interelectrode current i is equal to the emission current i_e .

For the particular case in which $i = i_0$ the valve is said to be *space-charge-saturated*. Any further increase of i_e causes now only a slight increase in i , and the valve is *space-charge-limited*. The ratio i/i_0 referred to as "degree of saturation" defines the three conditions; thus for space-charge saturation $i/i_0 = 1$, for temperature limitation $i/i_0 < 1$, and for space-charge limitation $i/i_0 > 1$. Figure 1 shows the usual {current, voltage} characteristic of a diode for constant emission current.

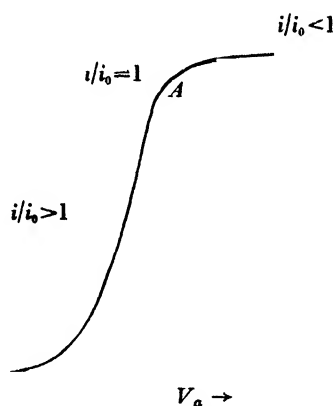


Figure 1. {Current, voltage} characteristic of a diode with constant emission current.

In this case the degree of saturation depends on V_a , which determines i_0 . At point A in the region of the upper bend $i/i_0 = 1$, to the right of this point $i/i_0 < 1$, and to the left $i/i_0 > 1$.

The static interelectrode conditions in the space-charge-limited diode have been examined by Langmuir⁽⁸⁾ and others^(9, 15). Since an initial velocity-distribution is implicit in this condition, the assumption made by the author in the treatment of the temperature-limited condition is no longer valid. Langmuir gives a complete solution for the voltage-distribution for any current greater than the saturation value and for any initial velocities. Owing to his rigorous treatment of the problem, however, it is a somewhat lengthy process to apply his solution to a practical case, and in the present paper Langmuir's results for the voltage-distribution are put into a more convenient form which lends itself to practical application. These results have then been extended to obtain the variation of the cathode field and of the electron transit time. A knowledge of the transit time in the space-charge-limited diode is of particular importance, since it has been shown⁽¹⁾ that the behaviour of a valve is dependent on electron transits not only at ultra-high frequencies

but also at the more normal low frequencies. The variation of cathode field is of interest in view of its possible effect on the emission, and on the maintenance of electron oscillations in the magnetron⁽¹⁰⁾.

§ 2. SUMMARY OF LANGMUIR'S TREATMENT

That part of Langmuir's paper referring to the space-charge-limited diode may be summarized as follows. Assuming that electrons are emitted from the cathode with normal components of velocity having a Maxwell distribution, Langmuir obtains, by integration of Poisson's equation between proper limits, a numerical relation between the variables ξ and η , where

$$\xi = 2(x - x_m) \left[\frac{2\pi^3 e^2 i^2 m}{k^3 \theta^3} \right]^{\frac{1}{2}} \quad \dots\dots(1)$$

and
$$\eta = \frac{e(V - V_m)}{k\theta} \quad \dots\dots(2).$$

Where x and V are the distance and voltage relative to the cathode, x_m and V_m give the position and voltage of the plane of minimum potential, i is the current passing between the electrodes, θ the absolute temperature, k the Boltzmann constant, and e and m have their usual meanings. ξ is positive when reckoned from potential minimum to anode, and negative from potential minimum to cathode. Langmuir's values of ξ as a function of η are given in the first three columns of the table.

Denoting values at the cathode by subscript 1 and reckoning distances and potentials from the cathode, we note that $x_1 = 0$ and $V_1 = 0$. Then

$$V = \frac{\theta}{11,600} (\eta - \eta_1) \quad \dots\dots(3),$$

$$(\xi - \xi_1) = 9.180 \times 10^5 \cdot \theta^{-\frac{3}{2}} i^{\frac{1}{2}} \cdot x \quad \dots\dots(4),$$

numerical values having been substituted for the constants.* Further it may be shown that

$$\eta_1 = \log_e \left(\frac{i_e}{i} \right) \quad \dots\dots(5),$$

where i_e (Langmuir's i_0) is the total emission current. Equations (3), (4) and (5) together with the tables of ξ enable the voltage-distribution to be computed for given values of θ , i and i_e . Thus these latter having been selected, the value of $-\xi_1$ as a function of η_1 , given by equation (5), is substituted in equation (4) and the ξ for a given x is obtained. The corresponding η substituted in equation (3) gives the required V_x .

Langmuir also gives as an approximate equation for the current

$$i = \frac{1}{9\pi} \sqrt{\frac{2e}{m}} \cdot \frac{(V - V_m)^{\frac{3}{2}}}{(x - x_m)^2} (1 + 2.66\eta^{-\frac{1}{2}}) \quad \dots\dots(6).$$

* Langmuir, using the electrostatic system for which the dielectric constant $\kappa = 1$, has omitted it from his equations.

η	$-\xi$	$+\xi$	$-\frac{d\xi}{d\eta}$	τ *
0.05	0.4281	0.4657	0.2448	0.4240
0.10	0.5941	0.6693	0.3605	0.5827
0.15	0.7167	0.8296	0.4564	0.6967
0.20	0.8170	0.9674	0.5426	0.7874
0.25	0.9028	1.0909	0.6230	0.8630
0.30	0.9785	1.2042	0.6997	0.9282
0.35	1.0464	1.3098	0.7740	0.9854
0.40	1.1081	1.4092	0.8465	1.0361
0.45	1.1648	1.5035	0.9177	1.0818
0.50	1.2173	1.5936	0.9881	1.1233
0.60	1.3120	1.7636	1.1280	1.1959
0.7	1.3956	1.9224	1.2676	1.2578
0.8	1.4704	2.0725	1.4084	1.3113
0.9	1.5380	2.2154	1.5513	1.3582
1.0	1.5996	2.3522	1.6972	1.3996
1.1	1.6561	2.4839	1.8467	1.4366
1.2	1.7081	2.6110	2.0004	1.4697
1.4	1.8009	2.8539	2.3223	1.5267
1.6	1.8813	3.0842	2.6673	1.5739
1.8	1.9515	3.3040	3.0391	1.6134
2.0	2.0134	3.5151	3.4418	1.6469
2.2	2.0681	3.7187	3.8796	1.6755
2.4	2.1168	3.9158	4.3571	1.7000
2.6	2.1602	4.1071	4.8789	1.7213
2.8	2.1990	4.2934	5.4503	1.7397
3.0	2.2338	4.4750	6.0769	1.7558
3.2	2.2650	4.6524	6.7651	1.7698
3.4	2.2930	4.8261	7.5216	1.7821
3.6	2.3183	4.9963	8.3540	1.7929
3.8	2.3410	5.1634	9.2705	1.8024
4.0	2.3615	5.3274	10.2801	1.8108
4.5	2.4044	5.7259	13.2815	1.8279
5.0	2.4376	6.1098	17.1193	1.8406
5.5	2.4634	6.4811	22.0344	1.8500
6.0	2.4834	6.8416	28.3352	1.8570
6.5	2.4990	7.1924	36.4170	1.8622
7.0	2.5112	7.5345	46.7876	1.8662
7.5	2.5206	7.8690	60.0982	1.8692
8.0	2.5280	8.1963	77.1851	1.8714
9.0	2.5382	8.8323	127.289	1.8745
10.0	2.5444	9.4465	209.88	1.8762
11.0	2.5481	10.0417	346.03	1.8772
12.0	2.5504	10.6204	570.53	1.8778
13.0	2.5518	11.1845	940.65	1.8781
14.0	2.5526	11.7355	1550.9	1.8783
15.0	2.5531	12.2747	2557.0	1.8785
16.0	2.5534	12.8032	4215.7	1.8786
18.0	2.5537	13.8313	11460	—
20.0	2.5538	14.8260	31150	—
25	2.5539	17.1931	—	—
30	—	19.4253	—	—
35	—	21.5522	—	—
40	—	23.5939	—	—
45	—	25.5643	—	—
50	—	27.4740	—	—
60	—	31.141	—	—
70	—	34.642	—	—
80	—	38.007	—	—
90	—	41.258	—	—
100	—	44.412	—	—
150	—	59.086	—	—
200	—	72.479	—	—
300	—	96.877	—	—
400	—	119.185	—	—
500	—	140.068	—	—
600	—	159.885	—	—
700	—	178.861	—	—
800	—	197.146	—	—
900	—	214.850	—	—
1000	2.5539	232.054	∞	1.8786

In this equation, i , i_s , and θ are known; η_1 and hence ξ_1 are found as before, and V_m and x_m are obtained by putting $\eta = \eta_m = 0$, and $\xi = \xi_m = 0$ in equations (4) and (5). Then for a given value of V , and hence of η , the corresponding value of x is found from equation (6). It will be seen that although equations (3), (4) and (5) contain the complete solution for the voltage-distribution, they are somewhat inflexible in form, and it is not easy to appreciate the correspondence of different sets of numerical results.

§ 3. TRANSFORMATION OF THE LANGMUIR EQUATIONS

Consider a pair of plane parallel electrodes separated a distance x_a , with the anode at a potential V_a relative to the cathode, and let the cathode emit a current i_s with an average velocity of emission u_0 , where

$$u_0 = \left(\frac{\pi k \theta}{2m} \right)^{\frac{1}{2}},$$

or, in terms of voltage,
$$V_0 = \frac{\pi}{4} \cdot \frac{k}{e} \cdot \theta \quad \dots\dots(7).$$

The current i , equal to i_s , which will pass between the electrodes when $V_0 = 0$ and $(dV/dx)_{x=0} = 0$ is given by

$$(i)_{V_0=0, dV/dx=0, x=0} = i_s = \frac{\kappa}{9\pi} \sqrt{\frac{2e}{m}} \cdot \frac{V_a^{\frac{3}{2}}}{x_a^2} \quad \dots\dots(8).$$

For the special case in which $V = V_a$ and $x = x_a$, equation (6) becomes

$$\frac{i}{i_s} = \frac{(1 - V_m/V_a)^{\frac{3}{2}}}{(1 - x_m/x_a)^2} \left\{ 1 + 3 \left(\frac{V_0/V_a}{1 - V_m/V_a} \right)^{\frac{1}{2}} \right\} \quad \dots\dots(6a).$$

It is interesting to note that when the cathode field is zero and $V_m = 0$, $x_m = 0$, then this equation coincides with one which was derived by entirely different treatment in the author's earlier paper⁽⁵⁾ and may be put in the form

$$(i)_{dV/dx=0, x=0} = i_0 = i_s \left\{ 1 + 3 \left(\frac{V_0}{V_a} \right)^{\frac{1}{2}} \right\} \quad \dots\dots(6b).$$

Now since i_0 can be obtained by measurement whereas i_s can only be obtained by calculation, it is of advantage to use i/i_0 as a parameter rather than the i/i_s of the earlier paper. Equation (6b) gives i_0/i_s , correct to within 1 per cent when $V_0/V_a < 0.01$, which is sufficient for all practical purposes.

Substituting V_0 and i_0 from equations (7), (8) and (6b) in equations (3) and (4) we obtain

$$\frac{V}{V_a} = \frac{4}{\pi} \frac{V_0}{V_a} (\eta - \eta_1) \quad \dots\dots(3a),$$

$$\frac{x}{x_a} = \frac{3}{\pi} \left\{ \left(\frac{V_0}{V_a} \right)^{\frac{3}{2}} \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a} \right)^{-\frac{1}{2}} \right\} \cdot \left(\frac{i}{i_0} \right)^{-\frac{1}{2}} (\xi - \xi_1) \quad \dots\dots(4a).$$

Equations (3a) and (4a) together with

$$\eta_1 = \log_e \frac{i_e}{i} \quad \dots\dots(5)$$

enable the voltage-distribution V/V_a as a function of x/x_0 to be easily obtained for given values of i_e , i/i_0 and V_0 .

The position and voltage of the plane of minimum potential are obtained by putting $\eta = \eta_m = 0$ and $\xi = \xi_m = 0$. Thus

$$\frac{V_m}{V_a} = -\frac{4}{\pi} \cdot \frac{V_0}{V_a} \cdot \eta_1 \quad \dots\dots(3b),$$

$$\frac{x_m}{x_a} = -\frac{3}{\pi} \left\{ \left(\frac{V_0}{V_a} \right)^{\frac{3}{2}} \cdot \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a^{\frac{1}{2}}} \right)^{-\frac{1}{2}} \right\} \left(\frac{i}{i_0} \right)^{-\frac{1}{2}} \xi_1 \quad \dots\dots(4b).$$

Taking into account the results of the next section, an examination of equations (3b) and (4b) shows that whereas the voltage of the potential minimum continues to increase logarithmically with increase of emission current, its distance from the cathode tends towards a maximum value dependent on V_0/V_a ; and this will not exceed a limiting value given by

$$\left(\frac{x_m}{x_a} \right)_{\max.} > 2.5 \left(\frac{V_0}{V_a} \right)^{\frac{3}{2}} \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a^{\frac{1}{2}}} \right)^{-\frac{1}{2}} \quad \dots\dots(4c).$$

§ 4. RELATION BETWEEN i/i_0 AND $\log i_e/i$

For a given electrode system i/i_0 depends only on V_0/V_a and i_e/i , and it is possible to obtain a family of curves showing i/i_0 as a function of η_1 , equal to $\log_e (i_e/i)$, with V_0/V_a as a parameter, one of the variables being thus eliminated from the equations.

If we put $x = x_a$ and $V = V_a$ in equations (3a) and (4a) and denote the corresponding values of η and ξ by the subscript a , we obtain

$$\eta_a = \frac{\pi}{4 (V_0/V_a)} + \eta_1 \quad \dots\dots(9)$$

and
$$\sqrt{\frac{i}{i_0}} = \frac{3}{\pi} \left\{ \left(\frac{V_0}{V_a} \right)^{\frac{3}{2}} \left(1 + 3 \sqrt{\frac{V_0}{V_a}} \right)^{-\frac{1}{2}} \right\} (\xi_a - \xi_1) \quad \dots\dots(10).$$

These equations enable i/i_0 to be calculated for any value of η_1 and for values of V_0/V_a less than 0.01. Curves for i/i_0 as a function of η_1 for constant values of V_0/V_a are shown in figure 2. By means of these curves we can now determine for given values of i_0 and V_0/V_a the total emission i_e required to give any anode current i , or vice versa; and it should be possible to devise a method, based on these curves, of

* This corresponds to the equation of Langmuir and Compton⁽¹⁵⁾, equation (313), which, however, owing to an arithmetical slip makes x_m only one-tenth of its correct value. Their equation should read

$$x_m = 16 (1000I)^{-\frac{1}{2}} \left(\frac{T}{1000} \right)^{\frac{3}{2}},$$

checking the total emission of a valve under normal working conditions without subjecting it to excessive anode voltages.

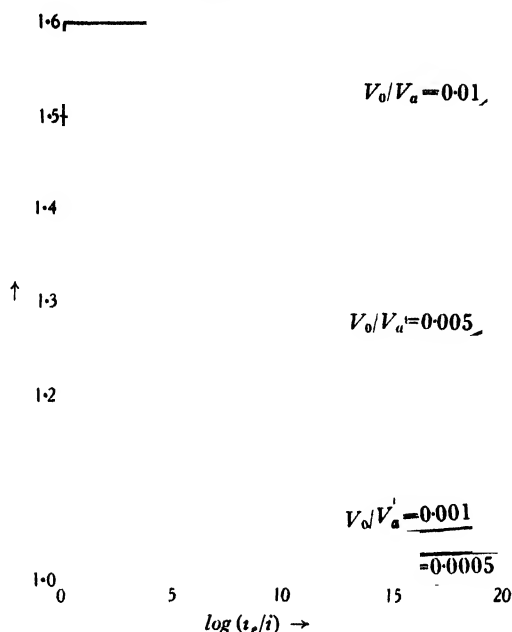


Figure 2. Variation of interelectrode current with emission current.

§ 5. VARIATION OF CATHODE FIELD

The variation of cathode field with current when $i/i_0 < 1$ was given in the earlier paper⁽⁵⁾ by an equation of the form

$$\left(\frac{dV}{dx}\right)_{x=0} = \frac{4}{3} \cdot \left(\frac{V_a}{x_a}\right) \cdot K,$$

values of K as a function of i/i_0 and V_0/V_a being tabulated.

For the sake of continuity, therefore, an equation of the same form is now derived for the case in which $i/i_0 > 1$. Differentiating equations (3a) and (4a), we obtain

$$\frac{\delta V}{V_a} = \frac{4}{\pi} \frac{V_0}{V_a} \delta \eta$$

$$\text{and} \quad \frac{\delta x}{x_a} = \frac{3}{\pi} \left\{ \left(\frac{V_0}{V_a}\right)^{\frac{1}{2}} \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a^{\frac{1}{2}}}\right)^{-\frac{1}{2}} \right\} \left(\frac{i}{i_0}\right)^{-\frac{1}{2}} \delta \xi,$$

$$\text{whence} \quad \frac{\delta V}{\delta x} = \frac{4}{3} \frac{V_a}{x_a} \cdot \left\{ \left(\frac{V_0}{V_a}\right)^{\frac{1}{2}} \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a^{\frac{1}{2}}}\right)^{\frac{1}{2}} \right\} \left(\frac{i}{i_0}\right)^{\frac{1}{2}} \frac{\delta \eta}{\delta \xi}.$$

$$\text{Then} \quad \left(\frac{dV}{dx}\right)_{x=0} = \frac{4}{3} \frac{V_a}{x_a} \cdot K \quad \dots\dots(11),$$

$$\text{where} \quad K = \left[\left\{ \left(\frac{V_0}{V_a}\right)^{\frac{1}{2}} \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a^{\frac{1}{2}}}\right)^{\frac{1}{2}} \right\} \left(\frac{i}{i_0}\right)^{\frac{1}{2}} \cdot \frac{d\eta}{d\xi} \right]_{\eta=1, \xi=1} \quad \dots\dots(11a).$$

Values of $d\eta/d\xi$ as a function of η_1 for the region between cathode and potential minimum have been calculated from Langmuir's results,* and are given in column 4 of the table. Since i/i_0 is a function only of V_0/V_a and η_1 , K is also a function only of V_0/V_a and of η_1 or i/i_0 . In figure 3, therefore, the variation of K with i/i_0 for various values of V_0/V_a is shown in the neighbourhood $i/i_0 = 1$. The results for cases in which $i/i_0 < 1$ have been taken from the earlier paper.

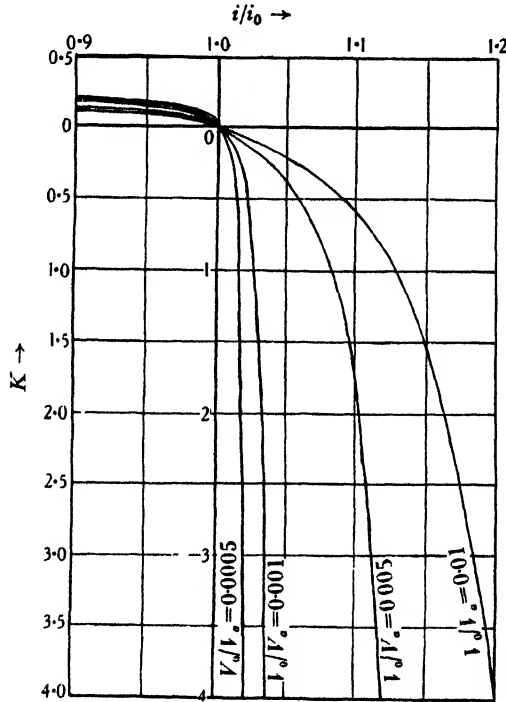


Figure 3. Variation of cathode field with current.

It will be seen that a negative value of cathode field, exceeding the maximum positive field for negligible current, can easily be obtained. Of course in practice i_c/i , and hence i/i_0 , is controlled by cathode-temperature, and variation of i/i_0 will therefore be accompanied by some variation of V_0/V_a .

§ 6. THE ELECTRON TRANSIT TIME

When electrons having a Maxwell distribution of velocities move through a retarding field the slower-moving electrons are continually being brought to rest and having their velocity reversed. It can be shown⁽¹¹⁾, however, that the forward-moving electrons still retain a Maxwell distribution, and it is then easy to prove that the average kinetic energy, and hence the average velocity, of the forward-moving

* Langmuir quotes

$$\frac{d\eta}{d\xi} = \left[e^\eta (1 + P\sqrt{\eta}) - \left(1 + \frac{2}{\sqrt{\pi}} \sqrt{\eta} \right) \right]^{\frac{1}{2}},$$

where

$$P(\sqrt{\eta}) = \text{erf } \sqrt{\eta} = \frac{2}{\pi} \int_0^{\sqrt{\eta}} e^{-\eta} \delta\eta.$$

electrons remains constant. This is due to the fact that although the retarding field continually reduces the velocity of all the electrons, the slower-moving ones are being continually filtered out. Thus the average velocity of electrons leaving the potential minimum for the anode is the same as the average velocity V_0 at the cathode, and since the field at the potential minimum is zero, the voltage-distribution up to the anode should correspond with that for a normal saturated diode. Regarding the potential-minimum therefore as a virtual cathode, we can apply the approximate equation of the earlier paper, equation (6*b*), to the virtual diode, provided that the voltage ($V - V_m$) and distance ($x - x_m$) be reckoned from the virtual cathode. On substituting the new value of i , equal to

$$\left(1 - \frac{V_m}{V_a}\right)^{\frac{3}{2}} / \left(1 - \frac{x_m}{x_a}\right)^2$$

of its value as defined by equation (8) we obtain

$$i_s = \frac{(1 - V_m/V_a)^{\frac{3}{2}}}{(1 - x_m/x_a)^2} \left\{ 1 + 3 \left(\frac{V_0/V_a}{1 - V_m/V_a} \right)^{\frac{1}{2}} \right\},$$

corresponding exactly with Langmuir's solution, equation (6*a*). We are therefore justified in applying the equations derived in the earlier paper for the case of space-charge saturation, to the region between potential minimum and anode; and this course will be adapted in calculating the transit time in this region.

The formation of the potential-minimum in front of the cathode causes an increase in total transit time. The variation of transit time with operating conditions is obtained by considering separately the transits from potential-minimum to anode and from cathode to potential-minimum.

§ 6.1. TRANSIT TIME FROM POTENTIAL-MINIMUM TO ANODE

It has been shown that at saturation the average electron transit time from cathode to anode is given by

$$T = 3 \sqrt{\frac{m}{2e}} \cdot \frac{x_a}{V_a^{\frac{1}{2}}} \left\{ \left(1 + \frac{V_0}{V_a} \right)^{\frac{1}{2}} + 2 \left(\frac{V_0}{V_a} \right)^{\frac{1}{2}} \right\} \quad \dots\dots(12).$$

Equation (12) gives the transit time of an average electron, i.e. one emitted with a velocity of V_0 volts. This differs from the effective average transit time by an amount which is usually negligible in practical examples.

When $i/i_0 > 1$, a potential-minimum is formed in front of the cathode and, as has been shown above, we may regard the potential-minimum as a virtual cathode emitting electrons with an average velocity V_0 equal to the average velocity at the true cathode. Furthermore we may assume the voltage-distribution between the virtual cathode and anode to correspond to that for a normal saturated diode. Thus equation (12) can be made to give the transit time T_a from potential-minimum to anode merely by changing the origin, and

$$\frac{T_a}{T'} = 3 \left\{ \frac{(1 - x_m/x_a)}{(1 - V_m/V_a + V_0/V_a)^{\frac{1}{2}} + 2(V_0/V_a)^{\frac{1}{2}}} \right\} \quad \dots\dots(13),$$

where

$$T' = 2 \sqrt{\frac{m}{2e}} \cdot \frac{x_a}{V_a^{\frac{1}{2}}} \quad \dots\dots(13a),$$

T' has been substituted for convenience and may be regarded as a parameter independent of the conditions of emission. With the help of figure 2, x_m and V_m can be calculated from equations (3b) and (4b), and equation (13) will then give T_a/T' as a function of i/i_0 , or of $\log_e(i_0/i)$, with V_0/V_a as a parameter.

For small values of V_0/V_a and η_1 , a convenient approximate formula can be derived. Thus substitution for x_m and V_m from equations (3b) and (4b) leads after some manipulation to

$$\frac{T_a}{T'} = 3 \left\{ \frac{1 - \frac{2}{\pi} \cdot \frac{V_0/V_a}{1 + 2(V_0/V_a)^{\frac{1}{2}}} \eta_1 + \frac{3}{\pi} (V_0/V_a)^{\frac{1}{2}} \{1 + 3(V_0/V_a)^{\frac{1}{2}}\}^{-\frac{1}{2}} (i/i_0)^{-\frac{1}{2}} \xi_1}{(1 + V_0/V_a)^{\frac{1}{2}} + 2(V_0/V_a)^{\frac{1}{2}}} \right\} \dots (13b)$$

when $V_0/V_a < 0.01$ and $\eta_1 < 5$, equation (13b) is in error by less than 0.5 per cent.

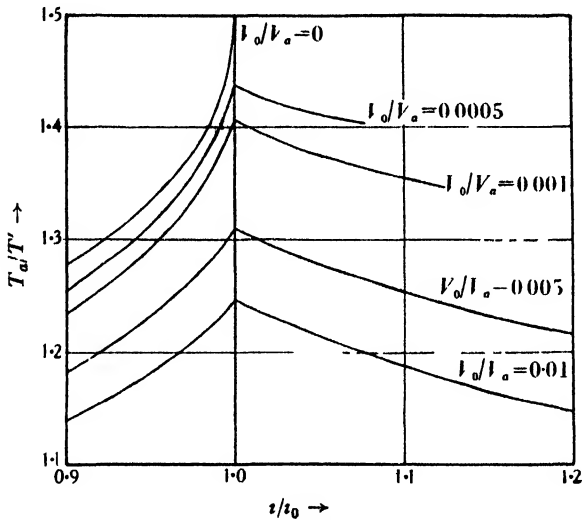


Figure 4. Variation of transit time from potential-minimum to anode.

In figure 4 are shown curves of T_a/T' as a function of i/i_0 , for constant values of V_0/V_a ; the values for cases in which $i/i_0 < 1$ are from the earlier paper⁽⁵⁾. The decrease of T_a/T' with i/i_0 is due partly to the movement away from the cathode of the potential-minimum, and partly to the increase of $-V_m$ causing an increase in the anode voltage relative to the potential-minimum.

§ 6.2. TRANSIT TIME FROM CATHODE TO POTENTIAL-MINIMUM OF ELECTRONS DESTINED TO REACH THE ANODE

The average transit time T_m from cathode to potential-minimum is here assumed to be the transit time of an average electron, i.e. of an electron which reaches the potential-minimum with a velocity of V_0 volts and which will have left the cathode, therefore, with a velocity of $(V_0 + V_m)$ volts. Since we are concerned only with those electrons which actually reach the potential-minimum and hence the

anode, this assumption is reasonably correct; although it must be used with reserve if alternating potentials also are present.

If for convenience we consider the potential-minimum as origin, an electron at a point x where the potential is V relative to the new origin will have a velocity u given by

$$\frac{1}{2}mu^2 = V_0e + Ve,$$

but

$$T_m = \int_{0, u_0}^{x_m, u_m} \frac{dx}{u} = \int_{0, 0}^{x_m, V_m} \sqrt{\frac{m}{2e}} (V + V_0)^{-\frac{1}{2}} dx.$$

Now again introducing the parameter T' , we find that

$$\frac{T_m}{T'} = \frac{1}{2} \left(\frac{V_0}{V_a} \right)^{\frac{1}{2}} \int_{0, 0}^{x_m, V_m} \frac{dx/x_a}{(1 + V/V_0)^{\frac{1}{2}}},$$

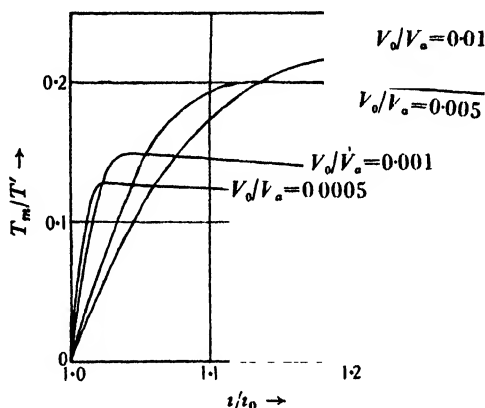


Figure 5. Variation with current of the transit time from cathode to potential-minimum.

but from equation (4a)

$$\frac{dx}{x_a} = \frac{3}{\pi} \left\{ \left(\frac{V_0}{V_a} \right)^{\frac{1}{2}} \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a} \right)^{-\frac{1}{2}} \right\} \left(\frac{i}{i_0} \right)^{-\frac{1}{2}} d\xi,$$

and from equation (3a)

$$\frac{V}{V_a} = \frac{4}{\pi} \eta_1,$$

since we are here taking the potential minimum as origin. Finally therefore

$$\frac{T_m}{T'} = \frac{3}{2\pi} \left\{ \left(\frac{V_0}{V_a} \right)^{\frac{1}{2}} \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a} \right)^{-\frac{1}{2}} \right\} \left(\frac{i}{i_0} \right)^{-\frac{1}{2}} \tau \quad \dots\dots(14),$$

where

$$\tau = f(\eta_1) = \int_{0, 0}^{\eta_1, \xi_1} \frac{d\xi_1}{(4\eta_1/\pi + 1)^{\frac{1}{2}}} \quad \dots\dots(14a).$$

The function τ has been calculated for various values of η_1 , and the results are given in column 5 of the table. Equations (14) and (14a) therefore give the variation of T_m/T' with i/i_0 , or i_e/i , for any value of V_0/V_a . Curves relating T_m/T' with i/i_0 for various values of V_0/V_a are shown in figure 5. It will be seen that for a given value of V_0/V_a , T_m/T' reaches a maximum and then very slowly decreases. This maximum is determined almost entirely by the movement of the potential-

minimum. From equation (14) and the tables of τ , an expression for the limiting value of T_m/T' can be obtained. Thus

$$\frac{T_m}{T'} \approx 0.90 \left(\frac{V_0}{V_a} \right)^{\frac{1}{2}} \left(1 + 3 \frac{V_0^{\frac{1}{2}}}{V_a} \right)^{-\frac{1}{2}} \quad \dots (14b).$$

It is at first surprising that the increase of $-V_m$ with i_e/i , and hence with i/i_0 , does not cause a more rapid decrease in T_m/T' . That it does not is due to the fact that for large values of i_e/i the greater part of the potential-drop is concentrated very close to the cathode; for the remainder of the region up to the potential-minimum the field is small and is practically unaffected by the increase of i_e/i . The transit time is therefore mainly affected by the slowly moving electrons in the region of the potential-minimum, where the velocity is not greatly different

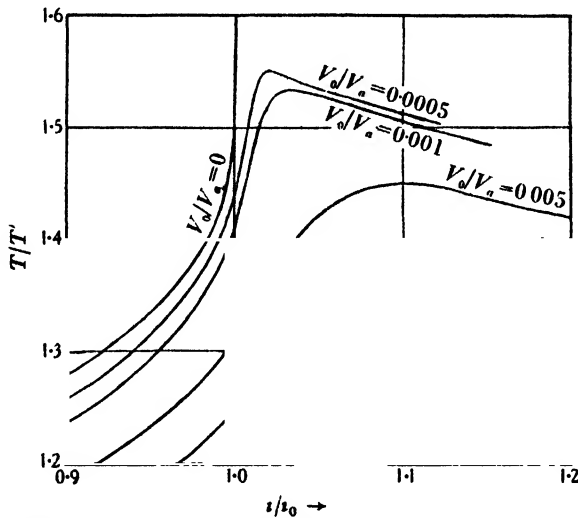


Figure 6. Variation of cathode-anode transit time with current.

from V_0 . It is due to the neglect of this fact that most earlier approximations for T_m have been too small.

The increase of T_m/T' with V_0/V_a is perhaps unexpected, since the average of the electron-velocity will increase with V_0/V_a ; it is due to the fact that the position of the potential-minimum also varies with V_0/V_a , and its distance from the cathode increases more rapidly than the velocity.

In figure 6 the results of the last two sections have been combined with those of the earlier paper to show the complete variation of cathode-anode transit time in the planar diode with variation of anode current. It will be seen that the curves for which $i/i_0 < 1$ join smoothly with those for which $i/i_0 > 1$, and this may be regarded

* D. O. North⁽⁴⁾ gives an expression, equation (14)

$$\frac{\tau_m}{\tau} = \frac{0.0016}{x_0} \left(\frac{5V_0}{\log_{10}(I_0/I)} \right)^{\frac{1}{2}} \left(\frac{T}{1000} \right)^{\frac{1}{2}} (1000I)^{-\frac{1}{2}}.$$

This is in error, since it is based on Langmuir and Compton's⁽¹⁵⁾ equation (313). Thus North's inequality of $\tau_m/\tau > 0.04$ for a typical case should be $\tau_m/\tau > 0.4$.

as evidence that the various simplifying assumptions made in each case are applicable within their correct limits to a degree of accuracy sufficient for most purposes.

§ 7. CONCLUSION

The voltage-distribution, the anode current, the cathode field, and the transit time in a space-charge-limited diode have been derived from the original equations of Langmuir by the use of his tables of ξ . The results have been given in the form of curves having, with the exception of those in figure 2, i/i_0 as the independent variable. Under certain circumstances, however, it might be preferable to use i_e/i_0 . In the condition of temperature limitation $i_e/i_0 = i/i_0$; for space-charge limitation, since $i_e/i_0 = (i_e/i)(i/i_0)$, the results can easily be adapted with the help of the curves of figure 2.

The theory has been worked out for plane electrodes, whereas in practice cylindrical electrodes are normally used. For the case of $i/i_0 = 1$, Langmuir⁽¹²⁾ has given an exact solution for the voltage-distribution with cylindrical electrodes, initial velocities being neglected; and he has also suggested⁽⁸⁾ an approximate solution for the case in which $i/i_0 > 1$, initial velocities being taken into account. Benham⁽¹⁾, Fortescue⁽¹³⁾, and McPetrie⁽¹⁴⁾ have calculated the transit time with cylindrical electrodes for $i/i_0 = 1$, initial velocities being neglected. The problem of cylindrical electrodes and finite initial velocities has hitherto defied exact solution. It is however reasonable to apply the results obtained here, qualitatively at least, to those conditions. It should be remembered, of course, that for a thin cathode the effect of initial velocities is much less owing to the greater concentration of field near the cathode. In cases where the electrodes are of nearly equal radii, the conclusions developed for plane electrodes may be used with confidence.

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THE RATE OF VISCOUS FLOW OF METALS: PART 1, TIN

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DISCUSSION

Dr BRUCE CHALMERS. Has the author given attention to the question of the purity of the material used, which is usually rather important? Further, tin is a metal in which the crystals readily grow to a large size, and may well be large enough to occupy the whole cross section of the wires used. Etching with ferric chloride solution serves to reveal the size and distribution of the crystals, and I should regard consideration of this point, as well as of the orientations of the crystals, as essential in work of this kind.

The conclusions drawn from figure 6 do not seem to be justified by the apparent accuracy of the points; the curve for 129° , for example, if examined on its own merits, would hardly be regarded as consisting of two straight lines.

I cannot agree with the contention regarding the 19° curves being affected by the $\alpha-\beta$ change, for the change takes place very slowly and is quite obvious. The photographs in figures 12*a* and 12*b* only show that in the latter the fracture took place where there was only one crystal in the cross section; they do not provide any evidence for the suggested $\beta-\gamma$ transition, but might perhaps tell us something about the conditions of strain and temperature necessary for re-crystallization into a single crystal. The same observation applies to the conclusions drawn from figure 15.

The discussion of the incidence of single and double glide appears to be invalidated by the absence of information as to the number and orientations of the crystals present; the effect of crystal boundaries on the stresses required to cause glide has been investigated by various workers, and should be taken into account in any theory based upon the results.

The careful and ingenious work described in this paper would be of greater value if it had been carried out under better defined conditions, and I think that a study of papers by Andrade, by Hanson and his collaborators, and by myself, appearing in the *Proceedings of the Royal Society* and the *Journal of the Institute of Metals* during the last few years, might be of interest to Dr Tyte when he is planning future work.

AUTHOR'S REPLY. The problem of distortion of metals has become of increasing interest in recent years, receiving particular impetus by the pioneer work of Carpenter, Taylor and Elam on the production and distortion of metal single crystals. Andrade and his school have done much interesting and valuable work along these lines, adding to our knowledge of the behaviour of single crystals and composite specimens of a few large crystals. However, the older method of attack, viz. that of investigating the properties of polycrystalline specimens, still remains of value. Dr Bruce Chalmer's criticisms appear to be mainly complaints that the

methods rightly adopted for the former type of experiment were not applied to the latter.

The experiments described in this paper were carried out in 1928 as part of an investigation of the variation with load and temperature of the velocity of flow of polycrystalline material in the form of wire. As far as I am aware, this investigation is the only one so far carried out on these lines, and the general character of the flow phenomena was naturally the prime object of the research. To this end, the material would appear to be adequately specified by its density and its preliminary treatment, which ensured strictly comparable specimens from experiment to experiment.

Now recrystallization from a few isolated growth centres, resulting in large crystals with orientations different from specimen to specimen, would naturally lead to very irregular behaviour. The best reply to Dr Chalmer's suggestion that this growth of large crystals took place in the specimens is offered by the marked regularity of the experimental results, not excepting the experiment at 129° C. Neither this, nor any other experiment, is expected to stand alone as conclusive evidence that the $\{\log_e v, p\}$ curves consist of two straight lines, but the cumulative evidence of the whole series makes this conclusion difficult to avoid.

The β - γ transition has been fairly widely reported in the literature; if Dr Chalmers is prepared to doubt its occurrence, any remark seems idle.

The specimens being polycrystalline in nature and the elementary grains distributed in a random manner, a discussion of behaviour on general grounds, found on this hypothesis, is perfectly justifiable and the agreement between the calculated and experimental ratios of the constants is unlikely to be fortuitous, confirmation on this point being offered by experiments on lead.

Finally, it may be stated that, although the phenomena have a personal character, as it were, in minor details for each metal investigated, the main conclusions drawn from the experiments on tin have been substantiated by experiments on lead and zinc. Accounts of this further work are shortly to be published.

THE MEASUREMENT IN ABSOLUTE UNITS OF THE INTENSITIES OF X-RAY REFLECTIONS FROM CRYSTALLINE POWDERS

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AND

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DISCUSSION

The remarks by Dr J. C. M. Brentano printed on page 107 of the present volume relate to the above paper and should have appeared on page 29.

REVIEWS OF BOOKS

A Text Book of Physics, by D. B. DEODHAR. Pp. iv + 672. (Allahabad: The Indian Press Ltd., 1937.) Rs. 6.

This is a courageous attempt to include between one pair of covers all the physics which an intermediate student requires, whether classical or modern. In the main it follows familiar lines, and it is divided into five water-tight parts each dealing with one of the branches into which physics is traditionally classified. In each section there has clearly been a definite effort to bring the subject up-to-date, and this is most conspicuously successful in the section on electricity.

The section on sound reads as though the author has himself confused the meaning of temperament with that of scale. Even after we have decided to adopt a pentatonic or diatonic or chromatic scale, or even Bosanquet's 53-tone scale, we have to decide on the exact intonation of each of the tones, and this is what decides the temperament. It is also to be regretted that in such an excellent book, with its real attempt to modernize teaching, there is no attempt to discuss architectural acoustics, a subject which would appear to lend itself rather well to qualitative explanation.

As has been stated above, the section on electricity is quite masterly, and manages to find space for wattmeters, generators, triodes and even the positron and neutron. It is to be hoped that the book will have the success which it deserves.

J. H. A.

Scientific Inference, by HAROLD JEFFREYS, M.A., D.Sc., F.R.S. Reissue with additions. Pp. vii + 272. (Cambridge: at the University Press, 1937.) 10s. 6d. net.

The additions are not likely to change anyone's opinion of this well-known book. They consist partly of a restatement of the author's main doctrine in the light of criticism directed against it, partly of minor amendments and corrections. But since there may still be some who have not read the book and yet would be interested by it, some brief description of its contents may be desirable.

Jeffreys's fundamental postulate is that knowledge derived from experience can be expressed in propositions each bearing a definite relation (its probability) to the data on which it is based, and that any such probability is either greater than, less than, or equal to any other. On this postulate he bases a logic of that part of physics which consists of numerical laws and mathematical theories and from it he derives rules by which the relative values of such propositions can be ascertained.

Many people believe that Jeffreys has solved completely the fundamental problem of scientific epistemology and that his work is truly epoch making. But that opinion is not universal. Some critics maintain that Jeffreys's conclusions are not logically sound and that his postulate will not bear the weight of the structure he builds on it; most of them have rival logics of their own, based on slightly different definitions of probability. The controversy is not, and probably will never, be ended; my personal opinion is that Jeffreys has the better of the argument, especially in counter-attack. Others simply disbelieve Jeffreys's postulate and all others at all similar to it. Their difference both from Jeffreys and from his critics is so profound that it is impossible to start an argument; Jeffreys naturally ignores them almost completely. But all, whether believers or critics, would agree on the profundity of Jeffreys's thought and on the brilliance of his exposition.

N. R. C.

Introduction to Physiological Optics, by J. P. C. SOUTHALL. Pp. x+426. (Oxford: University Press.) 21s. net.

This is in many ways a good book. It is attractively produced, and written in a style that is easy to read. Its scope is comprehensive for it includes some very useful chapters on refractive errors and their correction, in addition to discussions of binocular vision, rod-and-cone vision, colour vision and so on. It may certainly be regarded as a valuable reference book, so far as the earlier work on the subject is concerned, but perhaps the contents can be most readily appreciated from the fact that, as the author explains, "the material of the volume has been compiled from a course of lectures given in Columbia University over a long period of years". Possibly because the course had its origins so long ago the book gives the impression, in parts, of being old-fashioned.

Physiological optics is a subject that is very much alive at the present time. There are several important lines of work being developed in various laboratories in the United States and in Europe, lines that show every promise of converging to a point from which we may hope at last to see the whole complicated jigsaw pattern of visual phenomena fitting together to make one complete picture. We might reasonably expect to see some of this activity reflected in the book, but while we are given descriptions of many phenomena, references to recent work are extremely scanty. Nothing is said of the directional sensitivity of the retina observed by Stiles and Crawford, no reference is made to Lythgoe's work on visual acuity, there is no mention of the colour-blindness investigations of Pitt or of Trendelenburg and Schmidt, nothing of the measurements of retinal potentials or of nerve impulses by workers such as Granit, Graham or Hartline, and no reference to adaptation phenomena observed by the binocular method. In some ways perhaps the most surprising omission is that, in a section on colorimetry which includes references to the trichromatic system, colour triangles, transformation of colour co-ordinates from one system to another and so on, no indication is given of the existence of an internationally standardized system of colour specification approved some six years ago by the Commission Internationale de l'Éclairage. From the historical point of view the book is good, but as an up-to-date account of the subject it is far from complete.

W. D. W.

Textbook of Thermodynamics, by PAUL S. EPSTEIN. Pp. xii+406. (Chapman and Hall, Ltd.) 17s. 6d. net.

The authority of Epstein in the field of which this book treats is unquestioned, and the duty of the reviewer is merely to indicate the readers for whom it is intended, and perhaps to point out the features in which it differs from previous books on thermodynamics. As regards the first point, the author himself says that one half is intended for seniors and younger graduate students, whilst the other half is more advanced and could serve as a reference book. Turning then to the scope of the work, we find some new historical matter on the first law, and the usual insistence on the perfect gas. As regards real gases, the author considers that the warnings against the truth of the equation of Van der Waals have been overdone, and that a good word can now be said about it, in order to redress the balance. One other point of interest in his treatment of the fundamentals calls for remark: he postulates, and does not pretend to deduce, the principle of the decrease of internal energy, an attitude which is more honest or less confused than that of most writers on the subject. After the fundamentals have been established, the book deals in turn with applications to solutions and binary systems as well as to surface tension before dealing with Nernst's theorem, which is not entirely divorced from the quantum theory or from statistical mechanics. The degenerate gas is considered and forms an introduction to electronic problems, thence leading to specific heats, thermal radiation and electromagnetic phenomena. The book concludes with two critical chapters, of which the second is particularly valuable.

J. H. A.

Sound Waves, Their Shape and Speed, by DAYTON CLARENCE MILLER. Pp. xii + 164. (The Macmillan Co.) 12s. net.

Prof. Miller's phonodeik is well known to students of acoustics. In this comparatively small book, Prof. Miller describes, amongst other experimental work, various uses which have been devised for the phonodeik. That the author has attempted delicate acoustical investigations with a purely mechanical apparatus, consisting, as is well known, of a diaphragm with a mirror attached, shows not only great experimental ingenuity but also considerable courage. Most of us nowadays would demand a microphone, complicated amplifiers and expensive oscillographs for such work. The author's mechanical interests are still further shown in various digressions. The book should be read chiefly because of its historical interest, and also as a record of much patient investigation.

The book includes some hitherto unpublished work on the sound pressures in the neighbourhood of guns, another ingenious instrument, the baroscope, having been invented for this purpose. These experiments were made to determine whether the pressures in the explosion wave were responsible for shell shock. The interesting conclusion is reached that the air pressure acts upon the body much as a squeeze of the hand acts upon the bulb of a scent spray, the hydrostatic pressure in the skull being considerably increased thereby. This conclusion is in agreement with the observation that, in order to produce shock, the pressure pulse besides being of sufficient magnitude must also be of sufficiently long duration.

The book concludes with an account of measurements made to determine the variation of velocity of sound with its intensity, gunfire being used as a source of sound. It is shown that near a gun the velocity of sound can be as high as 2500 ft./sec., but that a few hundred feet away from the gun the velocity has fallen to its normal value.

The book contains a number of interesting photographs.

J. E. R. C.

Introduction to Ferromagnetism, by FRANCIS BITTER. Pp. xii + 314. (International Series in Physics. McGraw-Hill Publishing Co., Ltd. London.) 24s.

In recent years our knowledge of ferromagnetism has advanced rapidly in several widely divergent directions. New ferromagnetic alloys have been produced with properties that are, from the industrial point of view, greatly superior to those of any of their predecessors, while theories of ferromagnetism have advanced to the stage at which Prof. Bitter can say that "ferromagnetism as such is no longer fundamentally a mystery". Nevertheless the new materials have been discovered almost entirely by purely empirical methods, and we are still far from being able to account for the great range of properties obtainable with modern alloys, although studies of crystal structure and polycrystalline materials have led to important advances in this direction. Prof. Bitter takes the view that the important task for the immediate future is to "build a theory of alloys that will account for their properties about as well as the simple Weiss theory accounts for the magnetic properties of iron", and his book provides a broad survey of the present position of ferromagnetism from this point of view. It therefore includes an account of the theories of Weiss, Heisenberg, and Ising; a treatment of polycrystalline fields; discussions of the relations between magnetization and mechanical deformation, thermal, and electrical phenomena respectively; and a survey of co-operative phenomena (the formation of secondary structures and superlattices) contributed by F. Zwicky. On the purely practical side, there is a long and valuable chapter by T. D. Yensen on the methods of preparation, purification and analysis, which have been found specially valuable for the production of materials of very high permeability, together with a survey of modern industrial materials including alloys of high permeability and magnet steels. There is also an account by W. C. Elmore

of the powder technique for the investigation of the magnetic structure of the surfaces of magnetized materials, which is of great interest in connexion with the secondary structures associated with Zwicky's co-operative phenomena. It will be clear that the book puts the reader in touch with all the most progressive branches of the subject, and it has the merit of doing this without overburdening him with unnecessary detail, either theoretical or practical. The treatment is always such as to emphasize the physical basis of the mathematical theories and the points at which pure assumptions are made, while facts which are as yet unexplained are also clearly indicated. The book should prove of great value to many workers in the field between physics and metallurgy, in showing the connexion between their various activities. By revealing to new workers the possibilities of ferromagnetism as a tool for the investigation of the physical condition of alloys, i.e. internal strains and grain structure, it should form a definite contribution towards the study of the theory of metals.

L. H.

Low-Temperature Physics, by M. and B. RUHEMANN of the Physico-Technical Institute, Kharkhov. Pp. x+313. (Cambridge University Press.) 18s. net.

Sixty years ago Cailletet liquefied oxygen. At the time this event marked the successful culmination of half a century's unremitting effort to liquefy one of the so-called permanent gases. Faraday had pointed the way in 1823 when he liquefied chlorine, but the path was a stony one which had daunted the spirit of many an investigator. To-day we know that Cailletet's experiment has a greater significance, for it ushered in a new era of low-temperature research, and the volume under review surveys this fascinating field.

The book bears the address of Kharkhov, U.S.S.R. and it is interesting to note that a low-temperature laboratory there is equipped with hydrogen and helium liquefiers.

In their treatment the authors have followed the line of gradual penetration from such macroscopic phenomena as condensation and fusion to processes intimately connected with our concepts of elementary particles, such as give rise to magnetic moment and electrical conductivity. They have given particular attention to fields that have not yet been dealt with in a connected form, such as the subject of crystal structure stable at low temperatures. Considerable stress is laid on the principles of gas-liquefaction and rectification, and this is especially valuable as most of the work in this domain is not to be found within the scope of general physical literature.

The volume is divided into four parts. Part 1 deals with phase equilibrium, covering the topics of gas-liquefaction, the measurement of low temperatures, rectification, and solid-liquid equilibrium. Part 2 is devoted to the solid state and treats of the crystal lattice, the thermal energy of crystals, and Nernst's third law. Part 3 bears the title of orbit and spin. Here are discussed internal degrees of freedom, paramagnetism and magnetic cooling. In part 4 we have the free electron. This covers conductivity at low temperatures and supraconductivity.

Between December, 1935, when the book was written, and May, 1937, when the proofs were corrected, so many new facts came to light and so many papers were published that the authors have found it necessary to add five pages of references to the literature of this period. The book is very clearly written and the authors have rendered a valuable service to all interested in low-temperature physics by collecting and co-ordinating a vast amount of information. The volume will undoubtedly find a place in the library of every department of physics in our colleges as a valuable work of reference.

E. G.

Handbook of British Refrigeration Material 1938. Pp. 177. (The Cold Storage and Produce Review, Empire House, St Martin's le Grand, London.) 5s.

The object of the volume under review is to present the range of refrigeration materials that British manufacturers can supply. Although essentially a trade reference guide for the refrigeration industry, it should prove of considerable value to industrial physicists dealing with problems of thermal insulation, instrumental equipment and small refrigeration plants. The book includes a technical section in which the data required in refrigeration work are set out in tabular form. The appearance of this volume is a commendable sign of British enterprise in this field.

E. G.

Alternating Current Electrical Engineering, by PHILIP KEMP. Pp. x + 611. (London: Macmillan and Co.) 15s., 5th edition.

The appearance of a fifth edition of Mr Kemp's text-book on alternating-current engineering is sufficient evidence of its value to a wide circle of readers. Its success is due not so much to novelty of treatment as to the very clear way in which the essentials of the subject are presented, and to a wise selection of the material which has made the book representative of modern practice and has prevented the principles from being buried in a mass of descriptive detail and obsolete material. The 421 illustrations all consist of line drawings showing clearly the principles under discussion. No space is wasted on mere photographs showing external appearances only.

While the book is addressed mainly to students of electrical engineering, it can also be recommended to the many physicists who find it necessary to deal with such things as polyphase power supplies, synchronous and induction motors, transformers, rectifiers, and frequency-changers. At 15s. it is very good value.

L. H.

Frontiers of Science, by C. T. CHASE. Pp. xv + 340. (London: The English Universities Press, Ltd.) 12s. 6d. net.

This is a well-written book dealing with the most recent advances in astronomy, atomic physics, biochemistry and biophysics; some mention is also made of advances in chemistry and medicine. The Astronomer Royal remarks in his introduction: "The author's purpose is to describe what is being done rather than what has already been achieved, and to attempt to show where all this work is leading us."

The book contains 19 whole-page plates; the object of the inclusion of some of these is, however, obscure. It would have been better to include diagrams illustrating specific references in the text: for example on p. 47 an attempt is made to describe the Russell diagram in words—an almost impossible task without an illustration of it. In the chapter on relativity the author follows the general notion that the Michelson-Morley experiment and other attempts to detect ether-drift failed. As Dr C. V. Drysdale pointed out in a discourse before the Physical Society in 1935, this does not represent the facts.

In such a book more might have been said of the important advances made in branches of pure physics other than atomic physics, and in industrial physics; we hope that we may look forward to a further volume from the author's lucid pen covering these topics.

H. R. L.

The Science of Seeing, by MATTHEW LUCKIESH and FRANK K. MOSS. Pp. viii + 548. (London: Macmillan and Co. Ltd., 1937.) 25s. net.

The title of this book is the name used by the authors for a very wide field of knowledge which includes numerous topics belonging to about half-a-dozen of the more usually recognized divisions of science; namely, (1) purely physical topics, such as radiation, light sources, instruments, etc.; (2) electrical engineering, such as lighting installations and their maintenance; (3) optical, such as visual acuity, speed of vision and contrast sensitivity, to name only three of the many important topics of physiological optics; (4) pathological, such as long- and short-sightedness, inflammation of the eyes, digestive disorders, etc.; (5) physiological, such as nervous tension, eye-strain, headache, etc.; (6) psychological, such as impression, stimulation, confidence, etc. Thus defined, the science of seeing is, as the authors emphasize, more than a science of vision or a science of light utilization. In dealing with such a comprehensive subject within the limits of some 550 pages, the authors have confined the treatment to matters connected with the more recent knowledge of seeing, and have subordinated or excluded those aspects primarily developed in the relevant sciences named above. Accordingly, the discussions are largely concerned with controllable factors which can contribute to quick, certain and easy seeing, with a view to reducing the handicaps of unsatisfactory seeing conditions. This approach, which is to a large extent novel, cannot but be of great interest to all who are engaged on studies of vision, aids to seeing, or the relations of seeing to human efficiency, progress and welfare. Few, if any, investigators are better qualified to speak on this very wide and important subject than Luckiesh and Moss of the Lighting Research Laboratory of the General Electric Company at Cleveland, Ohio. They are well known both for their numerous papers and previous books on the subject, and also for several of the instruments and devices described in the present volume, such as their brightness meter, their visibility meter and Luckiesh's reflectance gauge. The text is accompanied by 84 tables of numerical data and 143 figures, all of which are well prepared and instructive, and many entirely original. The book ends with a useful bibliography of 184 books, reports and papers, and a good index (14 double-column pages); and a visibility indicator card is provided in a pocket affixed to the back cover.

W. J.

Light, Principles and Experiments, by GEORGE S. MONK. Pp. xi + 477. (New York and London: McGraw Hill, 1937.) 30s. net.

We learn from the preface that in the author's many years of teaching optics at the University of Chicago, he has always had to refer his advanced students to several different books for different branches of the subject, for lack of a suitable comprehensive work. The writing of this book is the outcome of that experience—an experience only too common, not only in his own country, but also in ours. Advanced students and their teachers alike will be grateful to Prof. Monk for this very useful and important addition to optical literature, which is both a text-book and a laboratory manual, as its subtitle is evidently intended to indicate. It is for students who have already worked through the equivalent of the Higher Schools or Intermediate Science syllabus of, say, London University, and are proceeding to work of pass or of honours B.Sc. standard. It is the second of the optical works of great merit and importance to come from the same press within a few weeks of one another. The first, Jenkins and White's *Fundamentals of Physical Optics*, with only 24 pages fewer than Monk's book, is devoted entirely to a restricted field, and has already been reviewed (p. 151) in this volume of our *Proceedings*.

The plan of the present work is admirable. In the first part, the text-book of 339 pages, there are (i) eight chapters (99 pages) on geometrical optics, dealing with fundamental

concepts, image formation, optical systems apertures, photometry, aberrations*, instruments and prisms; (ii) five chapters (150 pages) on those subjects that make up the classical physical optics, namely, the wave nature of light, velocity, interference, diffraction and polarization; (iii) three chapters (73 pages) on subjects that go to form the quantum physical optics, namely, spectra, the interaction of light and material media, and the effects of magnetic and electric fields; and (iv) a chapter (17 pages) on the eye and colour vision. A working knowledge of elementary mathematics including the differential and integral calculus is, of course, assumed, but as far as possible the author treats each topic in such a way that abstract mathematical development is subordinated to discussion of the physical principles involved. To this end, in some cases where the mathematical theory is beyond the scope of the book the results are quoted, while in other cases the derivations are given in appendices. While orthodox methods of presentation are usually adopted, there are several departures from it in novel illustrations and problems; and new advances, such as the recent progress in colorimetry, are discussed as far as the limits of the work allow. Well-chosen problems are set at the ends of chapters and the numerical answers are given at the end of the book.

The second, and much shorter, part of the book, is a laboratory manual (74 pages) consisting of precise working descriptions of twenty-three instructive experiments or groups of experiments. The book closes with a series of eight appendices to the text and to the experimental section, and six tables of useful data. The illustrations are numerous and good, and the index (17 double-column pages) is adequate.

W. J.

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THE STRUCTURE OF THE RETINA AND THE ROLE OF ITS VISUAL PURPLE

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The Thomas Young Oration delivered 9 December 1937

WHEN Thomas Young formulated his theory of colour vision, very little was known about the structure of the retina and the anatomical paths taken by the optic nerve to the brain: nothing at all was known about the nature either of the nervous impulse or of the photochemical processes in the retina. Physiology has made considerable advances during the last few years so that it is now possible to describe with some confidence the general nature of the processes which intervene between the impact of light on the retina and the consciousness of a visual sensation. The retina contains the layer of rods and cones, and it is in these elements that the light energy initiates the nervous impulse. The rods contain the substance visual purple which is bleached by exposure to light. So far as the rods are concerned we can say that the incidence of light on their visual purple results in some bleaching of this substance and that the bleaching process initiates a nerve impulse which eventually reaches the brain. No substance comparable with visual purple has been proved to occur in the cones, but the work of Wright⁽¹⁾ indicates that the physical process taking place in these structures must be similar in nature to that taking place in the rods. The nervous impulse eventually passes to the lateral geniculate body in the mid-brain whence it is relayed by another set of nerve fibres to the occipital cortex. That this is a true picture of the general scheme could have been stated more than twenty years ago, and progress since then has been in the nature both of an elaboration of the details and of greater assurance in the direction of further research. The purpose of this lecture is to show how recent work in anatomy, chemistry and physiology has helped to fill in the details of our general scheme linking the outside physical event with the inner consciousness of light. Nothing of what we say will be a direct contribution to the problem of colour vision, but by working out some of the details of achromatic vision, we shall have

narrowed the field of inquiry. We shall see the kind of physiological basis on which Young's theory of colour vision must rest.

Before proceeding any further we shall have to consider a most important advance in knowledge due to Schultze^(a), Parinaud^(3,4), and v. Kries⁽⁵⁾ and known as the duplicity theory. This theory has in effect given us two subjects for study where only one existed before, since it has drawn a line between the factors involved in vision at low illuminations and those involved at high illuminations. Most of the physiological developments have been concerned with the achromatic vision of low illuminations, but by increasing our knowledge of this type of vision we are really defining what still has to be explained in chromatic vision at higher illuminations. It will be necessary to give some account of the anatomy of the retina on which the duplicity theory is based.

The retina can be divided into three distinct regions, each of which has its own functions. The rods and cones which form one of these regions are sensitive to light. The nervous impulse initiated there passes through the second region, which is composed of layers of nerve cells and their nerve fibres, before it enters a fibre of the optic nerve. These layers can be likened to a complicated network for the sorting of nerve impulses. Finally, lying on the other side of the rods and cones, and farthest away from the incident light, there is the region known as the pigment epithelium of the retina. The pigment epithelium of many animals is remarkable for its richness in xanthophyll, a carotenoid pigment which may be concerned in the formation of visual purple. Although in most animals the pigment epithelium actually contains black pigment granules, in others they are absent. When present this black layer prevents internal reflections within the eye.

In most animals it is possible to distinguish both rods and cones in the retina, but owing to the diversity of form between different species it is not always possible to decide by its shape alone whether a given element is a rod or a cone. When both types of element are present in the same retina the distinction is usually easy. The retinæ of many animals appear on first sight to contain elements all of the same form and it is then often not possible to be sure whether these elements are all rods or all cones. The elements are, however, the terminal expansions of nerve cells whose nuclei form the outer nuclear layer of the retina, and although there may be great variety in the shape of the rod or of the cone amongst different animals, their nuclei differ uniformly from one another in that those of the rods are fuller of chromatin and stain more uniformly than those of the cones^(6,7). The rods also differ from the cones in containing the substance visual purple which can be brought into aqueous solution and whose presence can be demonstrated by histological stains. The new light-sensitive substance⁽⁸⁾ recently found in chickens' retinæ is present in very small quantities and it is not proved that it is present in their cones. Our ability to differentiate the two types of light-sensitive element will probably be surer when more is known about the differences in the electrical responses displayed by the retinæ of various animals⁽⁹⁾. There are unexpected and striking differences between the optical properties of the retina at high and low illuminations. Pencils of light entering the pupil through its centre produce a more luminous

sensation than those entering through other points provided the illumination is high⁽¹⁰⁾. At low illuminations all rays are equally efficient⁽¹¹⁾. This phenomenon may reflect a structural difference between rods and cones.

Schultze first observed that night-hunting animals had a predominance of rods, whilst day-hunting animals had the cone type of retina. This discovery was one of the most stimulating ever made in the study of the eye, but although no one would nowadays doubt its general truth it is nevertheless not the whole truth. Who, for instance, would guess that the cat, which catches a bird so well by day, has a retina almost exclusively composed of rods, whilst the owl with a similar retina sees with such apparent difficulty by day? The physiology of vision has suffered much from dogma and we should not attempt to explain too much on Schultze's observation; it would be rash to state that the rods played no part in vision at high, and the cones no part in vision at low illuminations. There can be no doubt, however, of the general truth of Schultze's observation, and we shall see that it has been given additional force by Kolmer's observations on retinal structure and habit in the monkeys.

There is no doubt that in ourselves visual sensations differ under high and low illuminations. When the relation between any visual capacity is investigated over a wide range of illuminations it is found that below about 0.01 ft.-can. there is one relation between illumination and the visual performance in question whilst above this figure another relation will hold. There may even be well-marked qualitative differences in the visual sensation, of which the Purkinje phenomenon is a good example. At low illuminations the spectrum is colourless and the greatest luminosity is at about 502 m μ . At high illuminations not only does the spectrum acquire the quality of colour, but the wave-length of greatest luminosity moves to 550 m μ . So fundamental is the distinction, that the terms "photopic" and "scotopic" are generally used to qualify vision under high and low illuminations respectively. The essential conception of the duplicity theory is, however, that the cones in our retinae are the organs for photopic vision and the rods the organs for scotopic vision. Since v. Kries's time every extended observation has emphasized this distinction between the subjective aspects of scotopic and photopic vision, but the connexion between the visual sensations on the one hand and the rods and cones on the other is not so satisfactory. If the graph relating a visual performance with illumination consists of two straight lines, it is easy to label one "rods" and the other "cones", but it is another thing to prove the relationship. As we shall see later, there are difficulties in the interpretation of experiments involving the peripheral retina. In these regions, although there are relatively few cones, vision is of the photopic type⁽¹²⁾; the peripheral retina behaves in the same manner as the central retina but with diminished sensitivity. In view of these difficulties it is of importance to see how far fresh objective evidence from the retina helps in the interpretation of visual sensation. Most of the matters to be considered in this paper are connected with scotopic vision and it will be convenient to summarize modern views on this subject. In scotopic vision we can see very feeble illuminations provided we have allowed sufficient time for our eyes to become adapted. Scotopic vision is colourless vision and in general is of an undifferentiated character. It lacks exact localization and

discrimination; Parsons⁽¹²⁾ has called it "dyscritic vision". Photopic vision, on the other hand, needs relatively high light-intensities, but once in action it is remarkable for its exactitude of localization and discrimination. Furthermore, visual acuity, the perception of movement and so on, improve progressively up to very high illuminations. The acme of achievement by photopic vision is the perception of colour. Photopic vision shows some changes during adaptation to darkness but it is sometimes difficult to know how these changes should be interpreted⁽¹³⁾.

The anatomy of the nervous layers of the retina cannot be neglected if we attempt to relate scotopic and photopic vision to the rods and cones respectively. One of the most firmly held views in the physiology of sensation is that the quality of a sensation is unalterably associated with the nerve fibre connecting the end organ to the brain. However we stimulate the nerve fibre arising from a cold spot on the skin, the sensation will always be one of cold. The only respect in which a sensory nerve fibre can vary its response is in the frequency of the impulses passing up it; any one impulse is no different from any other. Experimental evidence makes it clear that the change in frequency conveys the information of a change in intensity, but that, with the rather doubtful exception of the auditory nerve impulses, this change in frequency is associated with nothing else. All that is known about sensory nerves points to the conclusion that the chromatic sensations of photopic vision should pass to the brain along nerve paths which are different from those traversed by the nerve impulses conveying achromatic sensations. If the terms "photopic vision" and "scotopic vision" can be regarded as synonymous with "cone vision" and "rod vision", then we should expect to find separate nervous pathways for each in the retinal layer of nerve cells and nerve fibres. Ramon y Cajal believed that separate nervous pathways did exist and he described "rod bipolar" cells which were in contact with rods alone and "cone bipolar" cells which were in contact with cones alone. Presumably these rod bipolars and cone bipolars were the first sections of the separate paths of the rod and cone connexions with the brain. Polyak's recent work⁽¹⁴⁾ has failed to confirm this observation. He believes that although there are separate pathways for the impulses passing from certain cones, there are no such separate pathways for any rods. Although this evidence makes it difficult to interpret differences in the quality of sensations in terms of rods and cones, it does not affect the interpretation of other properties of vision in these terms. Let us suppose we have a rod and a cone each attached to the same fibre of the optic nerve. The frequency of the impulses arising from the rods by monochromatic illumination will depend on the light absorbed by the visual purple in the rods. We should expect the greatest frequency of nerve impulses to arise from a wave-length of $502\text{ m}\mu$. Monochromatic illumination of greater energy would stimulate the cones, and assuming that the response of the rods was swamped, the frequency of impulses would now be determined by the photochemical reactions of the cones and the greatest response would be at a wave-length of $550\text{ m}\mu$. The corresponding shift in the electrical response has been demonstrated by Granit and Wrede⁽¹⁵⁾. Our difficulty would lie in explaining why the rod gave rise to an achromatic sensation whilst the cone gave rise to a chromatic sensation.

There is another important capacity of the eye which has an obvious anatomical basis. I refer to its resolving power or the closely-related function of visual acuity. It is sometimes stated that each cone is served by a fibre of the optic nerve and that the bundles of fibres from the cones pass to the cerebral cortex, where they end in something resembling a telephone switchboard. A one-to-one relation is assumed. If this is true, then the resolving power of the retina must be limited by the fineness of the cone mosaic, the response in a single nerve fibre being the same whatever part of a cone is stimulated. For resolution of two points of light it is necessary that there shall be two stimulated cones with an unstimulated intervening cone. The need for the unstimulated cone will be realized when one considers that to an observer at the switchboard there would be no difference between two images of light stimulating two neighbouring cones and one larger image stimulating the same two cones. Such then is the theoretical explanation of the resolving power of the eye for two points. It is well supported by experiment, since it is found that the images of two points of light can be resolved provided they are not closer together than about $4\text{ m}\mu$. on the retina, whereas the diameter of the cones is just over $3\text{ m}\mu$. It will be noticed that no proof has been advanced that a one-to-one relation does indeed exist in the retinal layers, and it is only recently that Polyak has demonstrated the existence of a suitable anatomical basis.

Polyak used sections of the retinae from monkeys (*Macacus rhesus* or *M. mulatta*) and from an ape (chimpanzee), the eye of the latter probably being identical with that of man. The nuclei and fibres of the nerve cells were stained by Golgi's method. He found that in the region of the fovea there are specialized types both of bipolar cell and of ganglion cell which produce the desired one-to-one relation between the cone and the optic nerve fibre. The bipolar cells send out extensions towards the pedicles of the cones, and these extensions in most parts of the retina end in arborizations which make contact with the pedicles of many cones and rods. The type of midget bipolar which is found near the fovea sends out an extension which ends in a compact bouquet resembling "the half-open flower of the dandelion", and this bouquet is usually a little smaller than the single cone pedicle with which it makes contact. The opposite extension of a midget bipolar connects with one of the specialized individual ganglion cells which are found near the fovea. From the other extreme of the ganglion cell there arises the fibre of the optic nerve, which suffers only one further relay, in the lateral geniculate body, before reaching the cerebral cortex.

Here, probably, we have the retinal basis of the resolving power of the eye. It should be emphasized, however, that the histological technique is difficult, and it is a characteristic of the method used that only a small proportion of the cells takes the stain. It is not known how many of these one-to-one relations occur; certainly not all the cones in the central retina are connected in this way, although the proportion is high. In the rest of the retina many cones can be seen to be linked together by the extension of a common bipolar cell. Furthermore, in all parts of the retina, especially in its central parts, there are horizontal cells which connect a number of cones with one another. These horizontal cells have no central connexions. Apparently there are no horizontal cells for the rods.

Having noted that, except in the central retina, the one-to-one connexion of cone to nerve fibre is rarely seen, we find that we should have anticipated it. The total number of cones in the human retina is about 6,600,000⁽¹⁶⁾, but there are only 500,000 fibres in the optic nerve⁽¹⁷⁾. Each optic nerve fibre arises from a ganglion cell, and Pütter⁽¹⁸⁾ measured the ratio of the number of visual elements to the number of these ganglion cells. This he did for a great many animals, and he came to the conclusion that retinal resolving power depends less on the size of the visual elements than on the area of retina supplied by an optic nerve fibre (Innervationskreis) or the visual angle subtended by that area. We can explain resolving power at the fovea and its immediate surroundings in terms of the cone diameter, but the fovea occupies less than 1/10,000th of the area of the whole retina, and we have said nothing about the resolving power of the remaining parts.

In spite of Polyak's work we do not yet know enough to explain the resolving power of the non-central parts of the retina in terms of rods, cones and their connexions. There is, however, another approach open to us; we can calculate the number of nerve fibres needed by different parts of the retina in order to explain the resolving power of each of those parts. Since we know that the expected number of cones is present to explain the retinal resolving power at the fovea, we also know, assuming the one-to-one relation, the density of nerve fibres arising from that region. Knowing the resolving power of another part of the retina relative to the fovea, we can calculate the density of nerve fibres arising there. In other words, we divide the retina into zones and first calculate the number of fibres which would be needed in each zone if the visual acuity were unity, the value at the fovea. Secondly we multiply this number by the square of the visual acuity at the point in question.

The simplest way to make the calculation is to imagine the eye at the centre of a hollow hemisphere whose radius is 1 m. The hemisphere is then divided into zones, the latter being demarcated by lines subtending various angles to the line of vision

Table 1.

i Angle with line of vision (degrees)	ii Area of annular zone at 1 m. between angles (cm ²)	iii Number of nerve fibres on foveal basis (ii × 1100)	iv Linear acuity relative to fovea	v Necessary number of nerve fibres (iii × iv ²)
7½	415	4.6 × 10 ⁵	0.22	22,000
10	1190	1.3 × 10 ⁶	0.17	38,000
15	1650	1.8 × 10 ⁶	0.12	26,000
20	2100	2.3 × 10 ⁶	0.08	15,000
25	2530	2.8 × 10 ⁶	0.06	10,000
30	2940	3.2 × 10 ⁶	0.05	8,000
35	3340	3.7 × 10 ⁶	0.04	6,000
40	3700	4.1 × 10 ⁶	0.035	5,000
45	4040	4.4 × 10 ⁶	0.03	4,000
50	4350	4.8 × 10 ⁶	0.025	3,000
55			0.02	[13,000]
90				
			Total	150,000

which we suppose to pass through a pole of the hemisphere, table 1. For instance, lines making angles of 40 and 45 degrees will cut off an annular zone of the sphere whose area is 3700 cm², column ii. The fovea can resolve detail subtending 1' of visual angle, that is to say points which are separated by 0.03 cm. at 1 m. or areas of 0.0009 cm² at the same distance, and the retinal image of each of these areas would be served by one nerve fibre. An area of 1 cm² at 1 m. would contain about 1100 of these smaller areas, and the corresponding image on the retina would have to be served by about 1100 nerve fibres to account for resolution. If acuity at between 40° and 50° with the line of sight were unity there would be about 4,100,000 areas resolvable (3700 × 1100) in the annular zone, column iii, and the image of each area on the retina would need one nerve fibre. According to Wertheim⁽¹⁹⁾ the visual acuity for linear objects at this angle is only about 0.035, column iv, that at the fovea and the number of nerve fibres necessary to cover the area will be 4,100,000 × (0.035)², i.e. about 5000, column v. Proceeding in this way we can find the total number of nerve fibres necessary to explain the visual acuity at all points on the retina. Owing to the very rapid change of visual acuity in the region round the fovea it would be desirable to exclude this region from our calculation. Fortunately this is possible since we can calculate⁽²⁰⁾ that the central area of the retina subtending about 7½° in all directions with the line of fixation, is served by about 110,000 fibres of the optic nerve, leaving 390,000 fibres to serve the rest of the retina.

According to my calculations, using Wertheim's figures for peripheral visual acuity, about 150,000 fibres are needed to explain visual acuity between 7½° and 90°. With Fick's⁽²¹⁾ figures the number of fibres is under 100,000 whilst Dor's⁽²²⁾ figures give a still lower value. Owing to the fact that lack of practice and other factors are apt to lead to abnormally low values in judgments by the peripheral retina, the largest value is probably the best.

At the fovea and in the surrounding rod-free area visual acuity is certainly served by the cones alone for the simple reason that there are no rods present. For argument's sake let us assume that in photopic vision the cones alone serve visual acuity in the rest of the retina. There are about 600,000 cones in the central retina (up to 7½°), and if our assumption is true the 6,000,000 cones in the non-central retina must be served by 150,000 nerve fibres, that is to say there must be 40 cones to one nerve fibre. The 110,000,000 rods must be served by the remaining 240,000 fibres, that is to say there must be over 400 rods to one nerve fibre! This result is surprising and contrary to accepted teaching. Even if all the 500,000 fibres in the optic nerve were connected exclusively to the 110,000,000 or so rods there would still be more than 200 rods to one fibre. Actually the number of elements to each fibre is greater than the calculated value because of the overlap in distribution of the fibres. Furthermore, it is assumed that all fibres have the same function whereas the observable differences in diameter probably indicate that there are differences. The actual variation in size does not appear to have been worked out carefully for the human optic nerve, but in the frog it is considerable⁽²³⁾.

The calculation of the number of nerve fibres necessary to explain visual acuity for the whole of the external field of vision does not depend on any knowledge of

the size of the eye. All we need to know is the visual acuity for all points of the outside world and we can calculate the necessary number of nerve fibres. It follows that knowing the diameter of the optic nerve, we can form an approximate idea of an animal's visual acuity. If the diameter of the mouse's optic nerve were greater than that of the elephant, then the mouse would have the better visual acuity provided it had no refractive error.

The diameter of a rod is less than that of a cone, and since visual acuity cannot demand such a fine retinal mosaic it is difficult to see why the rods need be so small. The answer to many problems of the eye lies in comparative morphology and we will therefore consider the eye of the conger whose retinal elements are very different from our own. The conger has a retina almost exclusively composed of rods⁽²⁴⁾. Its optic nerve contains about 10,000 fibres⁽²⁵⁾ of varying diameter. The retina of a small conger has an area of about 64 mm², and assuming that the nerve fibres are evenly distributed over the whole surface, the retinal area served by one fibre will be a circle whose diameter is about 90 m μ . The diameter of one retinal rod in the conger is about 2 m μ . and in the circle there will be about 1600 rods to one nerve fibre, compared with about 400 in our own. Using as a basis the area of conger retina served by one nerve fibre it is possible to calculate the resolving power of the conger's eye, and we find that the smallest detail visible to the animal must subtend an angle of 1.6° compared with 1' in our own eyes at the fovea and about 25' in the mid-periphery.

The conger therefore has a large number of fine elongated elements in its retina and yet its ability to see fine detail must be poor. Why then does it need so many fine elements? It is found, in general, that amongst sea fishes the deeper the habitat the fewer the cones and more numerous and finer the retinal rods. Arey⁽²⁶⁾ explains this change by saying that it provides the animal with an improved visual acuity, but unless there is a corresponding increase in the number of nerve fibres, this cannot be the true explanation. My own belief is that the increasing fineness of the rods with depth of habitat leads to an increase in the carrying capacity of the retina for visual purple, the latter substance being adsorbed on the surfaces of the rods. In order to substantiate this statement it will be necessary to say something about visual purple.

Visual purple is a coloured substance found in the outer limbs of the rods and, so far as one knows, in no other retinal structure. It loses its colour on exposure to light, and provided it is in a healthy living retina, the colour is reformed in the dark^(27, 28). If the retina is placed in bile salts or in one of a number of other reagents which we will mention later, the visual purple is liberated into solution. When suitably purified the solution is red in colour with a bluish tinge when dilute. The colour bleaches in a few seconds in daylight. In solution there is only a small regeneration of colour in the dark.

Visual purple if not a protein itself is very closely associated with one. Its colour is destroyed by warming, by reagents such as ether and alcohol, and by strong acids and alkalis: its resistance to heat is increased by the addition of sodium chloride, and it is precipitated by full saturation with sodium sulphate at 30° C.

Its molecular weight is probably about 100,000 as determined by the ultracentrifuge⁽²⁹⁾. Diffusion methods suggest a molecular weight which is a submultiple of 810,000⁽³⁰⁾. All these properties suggest the protein nature of the substance. Other properties, however, do not appear at first sight to bear out this view. Visual purple is not destroyed by tryptic digestion, whereas it is by lipase. In addition it is not destroyed by weak potassium alum solutions or by weak formalin.

There is little doubt that the process of dark-adaptation is due to the reformation of visual purple in the eye after it has been bleached in the light. Man and animals suffering from a deficiency of vitamin A adapt to darkness more slowly than normal⁽³¹⁾, and it has been shown^(32, 33) that such animals do not regenerate their visual purple so well as normal animals. The retinæ of very many birds and fishes and amphibiae have been shown by Lönnberg⁽³⁴⁾ and Wald⁽³⁵⁾ to contain large quantities of xanthophyll. In the course of my purification of visual purple from *Rana esculenta* I obtained a yellow substance which Prof. Heilbron has kindly analysed and found to be xanthophyll. From the method used to obtain it, it is clearly either in the rods and cones, or in the pigment epithelium. If it is from the latter, as seems most likely, it must lie anatomically between the visual purple and the choroidal blood supply. The retina is also said to contain vitamin A⁽³⁵⁾. Wald has confirmed and extended these observations and has also described a new carotenoid substance, retinene. These and other observations leave little doubt that carotenes play an essential role in the formation of visual purple, and it is probable that one of these substances is an integral part of the visual purple molecule^(36, 35, 34, 37). Under certain conditions Wald finds that all three substances, namely, xanthophyll, retinene and vitamin A, are present in the retina simultaneously, but visual purple solutions contain only retinene. Wald has elaborated a hypothesis explaining the relation of these substances to the bleaching and reformation of visual purple. It should be pointed out, however, that the chemical facts are not yet firmly established⁽¹⁸⁾.

Visual purple can be liberated from the rods by most of the means used to liberate haemoglobin from red blood corpuscles, but whereas mechanical injury, thawing and freezing, and distilled water will haemolyse the corpuscles, they liberate very little visual purple from the rods. In order to obtain a satisfactory yield of visual purple Tansley⁽³³⁾ found it necessary in general to use what is known as a stromalytic agent, that is to say, one which can break up the envelope of the red blood cell and can presumably break up the envelope of the rod. Even so it is necessary to use a high concentration of the stromalytic agent in order to liberate the visual purple. A large number of such agents has been used, bile salts, bile acids⁽²⁷⁾, saponin and digitonin⁽³³⁾, and panaxtoxin⁽³⁹⁾. I have found that lysolecithin, the phosphatide prepared from cobra venom, will liberate visual purple in concentrations of 1 in 10,000. A concentration of 1 in 100,000 will haemolyse the red blood cells of a sheep⁽⁴⁰⁾.

The action of weakly alkaline solutions on the rods is interesting. In general such solutions cause a complete disintegration of tissues, and their action on the rods is no exception. I find that a M./20 buffer solution of pH10 will completely

disintegrate the cell structure of a suspension of rods, leaving only a mucoid mass in the test tube, but the visual purple will have passed into solution. The use of bile salts in addition to alkalis⁽⁴¹⁾ is unnecessary. Sometimes after the use of liquid air as an extractive, it is found that the visual purple centrifuges down after about 15 minutes at 4000 r.p.m. Such solutions are always slightly opalescent and on the acid side of neutrality. If, however, the solution is made alkaline, the opalescence disappears and the visual purple no longer sediments in the centrifuge. The interpretation I place on this observation is that the visual purple was originally adsorbed on the cell debris and that both sedimented together. When, however, the cell debris was disintegrated by alkali, the visual purple passed into true solution. Visual purple is easily adsorbed on alumina and animal charcoal without any demonstrable change in its absorption properties. In connexion with methods of preparation it may also be of interest to notice that visual purple is liberated from the rods by the negatively charged long-chain paraffin salt, palmityl sulphonic acid (sodium salt), which, if our interpretation is correct, competes with the visual purple for its place on the cell membrane. Visual purple solutions cannot be prepared by the use of cetyl pyridinium chloride, a similar but positively charged long-chain paraffin salt, but this substance acts as a very powerful haemolytic agent. The long-chain salts were given to me by the kindness of Dr G. S. Hartley.

On the whole the evidence suggests that visual purple is adsorbed on the rod envelope, but this can be regarded as little more than a suggestion. If true, it would give a reasonable explanation of the fact that deep-sea fishes, which live in very feeble illuminations, have a large number of fine rods.

It is not difficult to see that the deep-sea fish must rely relatively more on the presence of light and less on its fine localization than the surface forms. Adrian has shown that within limits the optic nerve impulses are identical, however the light is distributed in time and space on the retina. All that matters is that the product of illumination, area, and duration of flash should be kept constant. If many rods are served by one nerve fibre this result is understandable. Within narrow limits, however, the same is true for human foveal vision, namely that for a flash of light just to become visible it is necessary for the total quantity of light to be kept constant. At first sight this is difficult to explain when we remember that at the fovea there is a one-to-one relation of cone to nerve fibre. It has been shown by Polyak, however, that horizontal cells connecting the cones are present in all parts of the retina. These fibres bring small groups of cones into relation with one another in the central retina and produce interrelation of cones over a wider area in the peripheral retina. This is the probable anatomical basis of the integration of cone stimuli. No such horizontal cells were found to make contact with the rods, and so we must assume that the anatomical basis of the integration of rod stimuli lies in the ultimate concentration of many rods on one nerve fibre. In the conger retina it can be seen that the number of outer nuclei is very large, each cell to which the nucleus belongs also bearing one rod. There are far fewer bipolar cells, and this indicates that each of the latter is in connexion with many of the cells of the rods and cones. There is a still further reduction in the number of ganglion cells,

indicating a further concentration. A single optic nerve fibre arises from each ganglion cell and passes centrally. It is not known whether there is any further concentration in the lateral geniculate body.

One of the best pieces of evidence linking the rods and their visual purple with vision at low illuminations is found in the striking similarity between the scotopic luminosity curve and the absorption of visual purple at different wave-lengths. The density of visual purple in the dark-adapted retina is not known, but if it were very dense then it would appear quite black and it would absorb all wave-lengths completely. The scotopic luminosity curve would then be proportional to the number of quanta in different parts of the spectrum. If the visual purple had a density of 1.0 at 520 $m\mu$., it would absorb 90 per cent of the incident light, whilst the densities at 435 and 595 $m\mu$. would be about 0.13, that is to say about 10 per cent of the incident light would be absorbed. Suppose now that the concentration and therefore the density of the visual purple were increased ten times, a condition which would be produced by replacing one large rod by about 100 small ones. At 520 $m\mu$. practically all the incident light would be absorbed, as compared with 90 per cent before. At 435 and 595 $m\mu$. the density would be 1.3 and the visual purple would absorb about 95 per cent of these wave-lengths as compared with 10 per cent with the smaller concentration. The only considerable increase in absorption on increasing the density occurs towards the ends of the visible spectrum. One would expect from a knowledge of the absorption curve of sea water that in a clear sea only a narrow band of wave-lengths would be transmitted to the depths. This narrow band is centred around 520 $m\mu$.⁽⁴²⁾ which coincides with the maximum absorption of visual purple for some sea-water fishes. To such a fish lying in the dimly lighted depths the great potential increase in absorption at 435 and 595 $m\mu$. would be of no value because those wave-lengths would not be transmitted. The increased absorption would, however, be of great advantage to a fish living in muddy water or in an underground cave.

Deep-sea fishes may improve their vision in other ways, in particular by increasing the optical apertures of their eyes. It is found that of two closely related species, one will increase the aperture in this way and so achieve some vision, whilst another will have no eye, having evolved so as to depend on sense organs other than the eye.

In ourselves the process of adaptation to darkness occupies about the same time as the fading of daylight after the setting of the sun, so that we are ready for night when it comes. Many fishes and amphibia have a mechanism in their retinae which seems admirably adapted to protect the visual purple from bleaching should the animal find it necessary to come to the bright light of the surface waters. In feeble illuminations the retinal elements are so disposed that the incident light after passing through the nerve fibre layers comes first into contact with the rods and next with the cones, and finally it is absorbed by the black pigment epithelium. In higher illuminations, on the other hand, the sensitive elements change places so that the light after passing through the nerve fibres comes into contact with the cones, the organs of day vision, but it proceeds no further because the pigment

epithelium has advanced and there the light is absorbed. The rods lie behind and in the pigment and so their visual purple is not bleached even when light is shining into the eye⁽⁴³⁾. In our own eyes no such mechanism exists, useful as it would be in explaining some of the observations made on visual perception in the peripheral retina.

The tapetum is one of the most striking features of the eyes of many animals. Although there are three varieties, the commonest form is a layer of brightly coloured reflecting cells lying between the retina and the choroid. When a tapetum is present there are no heavily pigmented granules in the pigment epithelium. The presence of the tapetum is revealed very characteristically when one is motoring along a country road at night, the eyes of the animal shining brightly red or green. Its function, which at one time was uncertain, is more obvious since Kolmer's work on primates⁽⁴⁴⁾. This author found that a night-hunting form like *Nycticebus* has a retina in which rods predominate, whilst a day-hunting form like the macaque has a retina of the cone-type. The day-hunting forms have foveae for fine resolving power, but in the night-hunting forms these are absent and indeed they would be valueless in the low illuminations in which the animal is active. A tapetum could not be tolerated by a day-hunting form since it would result in considerable intra-ocular scattering of light and a lowering of the finer visual judgments. Every night-hunting Primate has a tapetum, however, and its probable function is to reflect back light which was not absorbed in its first passage through the visual purple of the rods, so making the greatest use of all the light which is available.

The remaining aspect of the economy of visual purple is its photochemistry and concerns the events between the absorption of light and the sensory impulse in the nerve fibre. Nothing is known about the way in which the bleaching of visual purple leads to a stimulation of the nerve endings. We do not know, for instance, whether stimulation occurs during the process of bleaching or by one of the products of bleaching, but recent work has widened our view of the bleaching process itself.

It is possible to measure the rate of bleaching of visual purple in monochromatic light by passing the latter through an optical cell containing the visual purple and then allowing it to fall on a photocell. As the visual purple bleaches the deflection of the galvanometer connected to the photocell increases⁽⁴⁵⁾. I do not propose to reproduce the analyses of the bleaching process but I should like to describe the final result. Owing to biochemical difficulties we do not know whether our solutions are of pure visual purple, and for that reason we do not know the value of the quantity α , the molecular extinction coefficient. From the bleaching experiments we can, however, calculate the product $\alpha\gamma$, where γ is the quantum efficiency of the reaction. This product at 505 m μ . has the value of about $9.0 \times 10^{-17} \text{ cm}^2$ ⁽⁴⁶⁾. For all known coloured substances α is rarely greater than about $10 \times 10^{-17} \text{ cm}^2$ except for those which have peak absorption bands. It follows that γ cannot be much less than unity. It would be possible for the value of α to be low and the value of γ to be greater than unity, but this can be excluded by another line of argument. If γ were greater than one, it would mean that after the absorption of a quantum by the molecule of visual purple, chain reactions occur involving other molecules, and if this were so the reaction velocity would be increased by a rise in

temperature. Hecht⁽⁴⁷⁾ has shown that the rate of bleaching remains *unaltered over the range 5 to 36° C. Recently we have extended the range of temperatures, and using conditions in which the mathematical treatment of the results is not invalidated by the behaviour of intermediate breakdown products, we find that the bleaching of visual purple by light is unaffected by temperature. We conclude that the quantum efficiency cannot be greater than unity, and since it is not much less, we can say provisionally that it is about unity.

So far as its photochemical properties are concerned, visual purple plays its role in the eye ideally, since with a quantum efficiency of unity each quantum absorbed will be effective in bleaching one molecule of visual purple. A quantum efficiency greater than unity, although it would produce a greater effect, might be of no advantage to the organism since chain reactions might be involved which were drawn out in time.

The general agreement between the scotopic luminosity curve and the absorption of light by visual purple at different wave-lengths has been known for many years and has attracted considerable attention. A remeasurement of the scotopic luminosity curve⁽⁴⁸⁾ revealed that the maximum of this curve was about 7 m μ . nearer the red end of the spectrum than the maximum of the absorption curve of visual purple. Dartnall and Goodeve⁽⁴⁹⁾ have shown, however, that the fit is extremely good if the luminosity curve is corrected on a basis of equal quantum and not equal energy. It is probable that the absorption of an equal number of quanta of any wave-length will lead to the bleaching of the same number of visual purple molecules and will produce the same sensation of brightness.

The electrical changes in the retina and optic nerve resulting from illumination of the eye have attracted much attention, but it is only recently with the work of Granit and his collaborators that the relation of these changes to the visual purple mechanism on the one hand and to the conscious sensation on the other hand has become at all clear. It is possible that in a few years' time we shall be able to trace the physical consequences of the impact of a weak light on the retina from the bleaching of the visual purple through the electrical changes in the retina to the impulses in the optic nerve which are finally presented to the occipital cortex. It is important to realize that the full correlation can be expected for weak light only. Granit^(50, 51) has shown that there is a good fit between the absorption curve of visual purple and the magnitude of the electrical response in the retina. Granit has also shown that certain phenomena of the critical frequency of flicker during light and dark adaptation⁽¹³⁾ are closely mirrored in the retinal potentials⁽⁵²⁾.

One of the stumbling blocks in the study of visual purple is the correct description of the bleaching process. Kühne⁽²⁷⁾ pointed out that during bleaching by light, a yellow substance (visual yellow) makes its appearance and that this in its turn becomes colourless. Whether or not visual yellow actually exists has been a much debated point, but it is now known^(53, 54, 55) that visual yellow is a substance with acid-base properties, and its detection by earlier workers depended on the hydrogen-ion concentration of their solutions. The substance was originally called "visual yellow" because it was thought to be sensitive to light and responsible for the blue-

sensation curve in colour-vision. Since this is no longer believed I prefer to call this substance "indicator yellow". Kühne said that during the bleaching of visual purple by light other colours appeared, one of which was orange. It is easy to demonstrate spectroscopically, that the orange colour is due not to a mixture of visual purple and indicator yellow, but to an intermediate form which is thermally unstable. Its exact position in the scheme of bleaching is uncertain but its existence is sufficiently obvious to justify a name and the one I have proposed is "transient orange".

A solution of visual purple has a maximum absorption at 502 $m\mu$. or so and the absorption becomes progressively less as far as 400 $m\mu$. but after that it begins to rise again. It is possible that the band centred on 502 $m\mu$. belongs to the light-sensitive grouping of the molecule whilst the absorption in the ultra-violet is due in part to impurities and in part to the protein portions of the molecule which may or may not be light-sensitive. It will be clear that one cannot determine the absorption curve of the light-sensitive part of the molecule from an unbleached solution since one does not know how much the various constituents of the solution contribute to density especially in the region 400 to 500 $m\mu$. It does not help to bleach the solution with light and to redetermine the absorption curve since newly formed chromophoric groups will have made their appearance. It is probable that the problem will be solved when one of the constituents of the complex, such as indicator yellow, has been isolated and purified, and when its absorption curve has been determined. On subtracting these values from the bleached curve, one will have the absorptions of the light-stable part of the molecule and impurities, whilst on subtracting these derived values from the densities of the unbleached solution one will find the densities of the light-sensitive part of the molecule. At the moment it is possible only to guess at the densities of the light-sensitive portion⁽⁵⁵⁾.

Although the yellow products of bleaching do not appear to play any direct part in vision by being sensitive to light, it is possible that they modify vision by acting as internal filters absorbing the shorter wave-lengths. With a high illumination of the retina most of the visual purple would be bleached, and unless it was removed there would be considerable accumulations of yellow substances. This state of affairs might seriously modify the luminosity curve obtained from the rods, but before examining this possibility let us inquire more closely into the Purkinje phenomenon.

The scotopic luminosity curve measured at very low illuminations follows the absorption curve of visual purple, and there can be little doubt that the retinal rods are the percipient organs involved. The duplicity theory teaches that the photopic luminosity curve is mediated by the cones. Since at an angle of 18° in the peripheral retina there are about 30 rods to 1 cone⁽¹⁶⁾ we might expect the luminosity curve to be of the scotopic type or at least to show some traces of its rod parentage. As Parsons⁽¹²⁾ says (p. 177): "One of the greatest difficulties, hitherto unsurmounted, of the duplicity theory is the behaviour of the periphery of the field of vision. There is overwhelming proof, derived from peripheral luminosity curves, minimal field and minimal time luminosity curves, that peripheral vision behaves in exactly the same manner as central vision, but with diminished sensitivity." In the perception

of flicker at high illuminations the peripheral retina also behaves like the central retina but with decreased sensitivity⁽⁵⁶⁾ provided large areas are not used⁽¹³⁾.

The scotopic luminosity curve has a maximum at about $502\text{ }\mu$, but if the determination is made at increasing illuminations the maximum of the curve moves slowly to about $550\text{ }\mu$. when corrected on the quantum basis. We might say that during the increase in illumination the cones are stimulated more and more, and for that reason their characteristics assert themselves at the expense of the rods. In view of the difficulties encountered in the peripheral retina it might be profitable to ask whether the known properties of visual purple and its breakdown products could play any part in the Purkinje phenomenon.

At very low illuminations the luminosity curve will fit the curve for the quantity of light absorbed by a weak solution of visual purple at different wave-lengths. As the illumination of the retina is raised, so also will the breakdown of visual purple be increased. If the yellow products of bleaching were not immediately removed from the rods they would function as yellow internal filters and under certain conditions would protect the visual purple from the action of the shorter wave-lengths, so shifting the maximum absorption of light towards the longer wave-lengths. Holm⁽⁵⁷⁾ believed that the yellow products of bleaching were produced in larger amounts at high illuminations and acted as protective filters to the visual purple. Walls and Judd⁽⁵⁸⁾ have found yellow substances in the eye tissues of many animals and believe them to be protective. If the yellow products of bleaching are protective, it must be a protection which is selective for the near ultra-violet and the shorter visible wave-lengths. If the yellow products of bleaching were removed only slowly, their concentration would increase as the illumination of the retina was raised, but the concentration of visual purple would decrease and if the optical densities were not too low, there would be a progressive shift in the luminosity curve. This process could not go on indefinitely because the wave-length of maximum luminosity would pass farther and farther towards the red end of the spectrum whereas we know that it does not pass beyond about $550\text{ }\mu$. One would have to assume that above certain illuminations an equilibrium is reached between the breakdown of visual purple, the removal of the yellow products and reformation of visual purple.

The published absorption curves of visual purple are accurate enough for our purpose, but the hydrogen-ion concentration of the retina is rather doubtful, and since indicator yellow varies in colour with pH it is difficult to know which values to use for the density of this substance.

In addition it is possible that the pH of the retina is lowered on illumination, and this presents a further difficulty. In the calculation which follows I have assumed a pH value for the retina of 6.5 and have used my own absorption curve for indicator yellow⁽⁵⁵⁾.

Let us assume that at a certain high illumination the concentration c' of indicator yellow is 100 times that c of visual purple. If the extinction coefficients of the visual purple and of the indicator yellow are α and α' respectively and l is the length of the rod, then the optical density of the visual purple will be αcl and that of the indicator

yellow will be $\alpha'c'l$ or $100\alpha'cl$. Of the total light absorbed at any one wave-length, visual purple will absorb

$$\frac{\alpha cl}{\alpha'c'l + \alpha cl}, \text{ or } \frac{\alpha}{100\alpha' + \alpha}.$$

If the incident light is I_0 , then the total absorbed light is given by

$$I_0 (1 - 10^{-\alpha cl - \alpha'c'l})$$

and the light absorbed by the visual purple alone is given by the expression

$$\frac{\alpha I_0}{100\alpha' + \alpha} (1 - 10^{-\alpha cl - \alpha'c'l}).$$

If we express I_0 in quanta and consider an equal-quanta spectrum, then we can easily calculate the value of the expression at every wave-length. The values so obtained will give the number of quanta absorbed by visual purple at each wave-length and probably the values for the luminosity curve.

If the retinal absorption is very small the light absorbed by the visual purple is

$$\frac{\alpha I_0}{100\alpha' + \alpha} (\alpha cl + \alpha'c'l) = I_0 \alpha cl,$$

that is to say it is proportional to the density of the visual purple and is independent of the presence of indicator yellow. If, on the other hand, the retinal density is very high, then the light absorbed by the visual purple is

$$\frac{\alpha I_0}{100\alpha' + \alpha}$$

and the effect of the indicator yellow will be considerable. It is probable that neither of these conditions obtains in the retina and for the sake of an example we will assume that the density αcl of the visual purple at 502 m μ . is 0.02. The densities at other wave-lengths are taken from the absorption curve of visual purple⁽⁵⁵⁾ and are given in column ii in table 2. The densities of indicator yellow at 100 times the

Table 2.

i Wave-length (m μ .)	ii D_{VP} ($\times 100$)	iii D_{IY} ($\times 10$)	iv I_t on the assumption $I_0 = 100$	v Radiation absorbed by visual purple
420	0.40	9.0	12.5	0.39
440	0.85	6.8	20.5	0.98
460	1.34	5.1	30.0	1.80
480	1.76	3.6	41.9	2.70
490	1.92	3.0	47.9	3.14
497	1.98	2.5	53.7	3.40
502	2.00	2.3	56.2	3.50
510	1.94	1.9	61.7	3.55
520	1.80	1.5	67.9	3.43
530	1.56	1.1	74.8	3.12
540	1.24	0.8	80.8	2.57
560	0.62	0.4	89.9	1.36
580	0.22	0.1	97.2	0.50

concentration of the visual purple can be calculated from the graph given in the same paper⁽⁵⁵⁾, and at 502 m μ . the density will be about 0.230 at a pH of 6.5. Densities at other wave-lengths are given in column iii. Assuming that in a given time the radiation at each wave-length is 100 quanta one can calculate the radiation transmitted by the retina, column iv, from which one can calculate the light absorbed by the visual purple alone. These figures are given in column v. It will be seen that the greatest amount of light is absorbed no longer at 502 m μ . but nearer 510 m μ ., and it is at the latter wave-length where we would expect the spectrum to be most luminous. By assuming that transient orange with its much more prominent short-wave absorption is present in large quantities in the retina and by assuming very low concentrations of visual purple, endless possibilities are offered to a skilled computer. It should not be difficult to force the wave-length of maximum absorption as far as 550 m μ .

It seems improbable to me that yellow breakdown products are present in sufficient concentrations to produce more than a small shift in maximum luminosity. There is also some evidence to show that at least two different photochemical substances are simultaneously present in the retina. König found from the measurement of luminosity curves at various levels of illumination that although there was a gradual shift of the wave-length of maximum luminosity, the luminosity curves at intermediate illuminations were not smooth curves. There was plain evidence that two processes were contributing to the final brightness and for simplicity we will say that both the rods and the cones were active at these intermediate illuminations each adding a contribution to the final luminosity. At illuminations just above those for pure rod vision there was a bulge on the luminosity curve towards the longer wave-lengths, presumably due to the cones, whilst at higher illuminations the curve appeared to be of the all-cone type except for a bulge on the short-wave side. The curves for retinal potentials are equally striking and show the influence of cone vision at illuminations very little higher than the smallest which will produce any electrical response at all⁽⁵⁰⁾.

Disappointing though it is, we are forced to admit that we cannot find a role for visual purple in vision at high illuminations. What evidence there is indicates that the visual purple is present and must be undergoing continuous bleaching in the living eye under high illuminations, but vision shows no scotopic components under these conditions. Furthermore, even though the cones are numerically far inferior to the rods in the peripheral retina, the responses of these regions are nevertheless of the pure photopic type. Our conclusions must be that visual phenomena are interpretable under conditions of scotopic vision but that we are as far as ever from finding a material basis for phenomena of photopic vision and the mechanism of colour vision.

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THE FUNDAMENTAL UNIT OF ELECTRIC CHARGE

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ABSTRACT. A generalization of the uncertainty relationships for the case in which an electromagnetic field is present is developed. It is further shown that the atomicity of electric charge is a consequence of the integral relationships which are a feature of the quantum theory.

IT is well known that the equations of motion of a charged particle in an electromagnetic field can be expressed in the same form as those of a geodesic when we replace the old generalized momentum, \mathbf{p} , by a new momentum

$$\mathbf{\Pi} = \mathbf{p} + \frac{e}{c} \boldsymbol{\phi},$$

in which $\boldsymbol{\phi}$ is the electromagnetic vector potential and e is the charge on the particle⁽¹⁾. They do not however represent a geodesic in the space-time continuum—except when $\mathbf{\Pi} = \mathbf{p}$ —and hence Kaluza⁽²⁾ added a further dimension to that of space-time, thus constructing a continuum in which the paths of charged as well as those of uncharged particles were geodesics. This more extended momentum, $\mathbf{\Pi}$, was introduced into the familiar conditions of the older quantum theory. Thus the relations

$$\oint \mathbf{p}_m dq_m = n\hbar, \quad (m = 1, 2 \text{ or } 3)$$

which could only be applied in the absence of a magnetic field, became⁽¹⁾

$$\oint \mathbf{\Pi}_m dq_m = n\hbar \quad \dots\dots(1).$$

The importance of this modification is evident in its application to the Zeeman effect. Its importance in the new quantum dynamics has been emphasized by Gordon. It will be remembered that in Schroedinger's theory the momentum component p_m is replaced by the operator

$$\frac{\hbar}{2\pi i} \frac{\partial}{\partial q_m}$$

in Hamilton's equation. Gordon pointed out that in the more general case it is Π_m which should be replaced by this operator.

In other words p_m must be replaced by

$$\left(\frac{h}{2\pi i} \frac{\partial}{\partial q_m} - \frac{e}{c} \phi_m \right).$$

Dirac in his electron theory substitutes

$$\left(p + \frac{e}{c} \Phi \right)$$

for p ; in this case e denotes the charge of the electron. A feature of the later quantum dynamical theory is the uncertainty relationships

$$\Delta p_m \Delta q_m \sim h, \quad \Delta W \Delta t \sim h \quad \dots\dots(2),$$

in which the values of m are 1, 2 or 3 and, if we use the notation of the theory of relativity, we can write equations (2) in the single statement

$$\Delta p_m \cdot \Delta x_m \sim h \quad \dots\dots(3),$$

in which m has the values 1, 2, 3 or 4.

When an electromagnetic field exists equation (3) must, it is clear, be generalized to take the form

$$\Delta \Pi_m \cdot \Delta x_m \sim h \quad \dots\dots(4).$$

The fourth of these, for example, is identical with

$$\Delta (mc^2 + eV) \Delta t \sim h \quad \dots\dots(5),$$

where V is the ordinary scalar potential, $(mc^2 + eV)$ denoting the total energy W of the particle.

Kaluza replaced the square of the interval ds^2 , equal to $g_{mn} dx^m dx^n$, which is characteristic of the Riemannian geometry of the space-time continuum, by $d\sigma^2$, equal to $\gamma_{\mu\nu} dx^\mu dx^\nu$. The coefficients $\gamma_{\mu\nu}$ are of course different from the g_{mn} and they are more numerous. We require to note the values of those coefficients only in which the subscript 5 occurs:

$$\gamma_{m5} = \gamma_{5m} = \gamma_{55} \alpha \phi_m \quad \dots\dots(6),$$

while the contravariant ones are:

$$\gamma^{m5} = \gamma^{5m} = -\alpha \phi^m \quad \dots\dots(7),$$

α being a new constant characteristic of Kaluza's theory.

In Einstein's relativity the momentum component p_m , of a particle, may be written

$$p_m = m_0 g_{mn} \frac{dx^n}{d\tau},$$

in which m_0 is the rest mass of the particle and $d\tau$ is the element of proper time defined by

$$ds^2 = -c^2 d\tau^2.$$

The extended momentum Π_m is expressed by

$$\Pi_m = m_0 \gamma_{m\nu} \frac{dx^\nu}{d\tau} \quad \dots\dots(8).$$

The familiar summation is implied in both definitions; but while the summation with respect to n in the former extends from 1 to 4, the summation with respect to ν in the latter extends from 1 to 5. In Kaluza's theory we have of course a fifth component

$$\Pi_5 = m_0 \gamma_{5\nu} \frac{dx^\nu}{d\tau} \quad \dots\dots(9),$$

and when we identify this component with charge divided by αc , or $q/\alpha c$, the equations of motion of the charged particle become those of a geodesic⁽³⁾. It may be noted that the conservation of the momentum Π includes the principle of momentum in its narrower sense as well as that of mass, energy and charge.

The incompleteness of the uncertainty relationships (4) is now easily removed, for the appearance of $q/\alpha c$ as a momentum with the implied inclusion of the conservation of charge in a generalized principle of conservation of momentum suggests and indeed requires the further uncertainty relationship:

$$\Delta \Pi_5 \Delta x^5 \sim h \quad \dots\dots(10).$$

Now we can learn nothing about x^5 by any measurement and therefore the uncertainty, Δx^5 , is infinite and $\Delta \Pi_5$ consequently zero. This simply means that under all circumstances there is no limit to the precision with which Π_5 , and therefore also q , can be known.

The co-ordinate x^5 occurs in a very restricted way in the theory of Kaluza and Klein. It has in fact the character of a cyclic co-ordinate. The corresponding momentum Π_5 is constant and enters the wave equation through the factor

$$e^{(2\pi i \Pi_5 / h) x^5}.$$

We may compare the co-ordinate x^5 with the co-ordinate θ of a rigid body rotating about a fixed axis under no forces, and Π_5 with the corresponding momentum, p_θ . It is well known⁽⁴⁾ that

$$p_\theta = nh/2\pi,$$

a result which can be derived from the old quantum condition

$$\oint p_\theta d\theta = nh \quad \dots\dots(11).$$

The corresponding condition involving Π_5 and x^5 is

$$\oint \Pi_5 dx^5 = nh \quad \dots\dots(12)$$

or

$$\Pi_5 l_0 = nh,$$

where l_0 is some fundamental periodic length of x^5 . Therefore

$$\frac{q}{\alpha c} l_0 = nh$$

or

$$q = n h \alpha c / l_0 \quad \dots\dots(13).$$

Hence a charge is made up of integral multiples of a unit e which is equal to $\alpha h / l_0$.

Thus the atomicity of charge is the outcome of the integral relationships which have been an essential and characteristic feature of the quantum theory since the

constant h was introduced by Planck. The application of Kaluza's theory made by Klein in his description of the quantum theory suggests that l_0 may be conveniently replaced by h/m_0c . This means that we replace the fundamental constant l_0 by another, m_0 , of the dimensions of mass. We now obtain from equation (13) the result that the ultimate unit of electric charge may be expressed by

$$e = \alpha m_0 c^2 \quad \dots\dots(14).$$

If the value of α thus obtained be introduced into Kaluza's theory, we find that the geodesic represents the motion of a charge e associated with mass m_0 in an electromagnetic field. Thus m_0 naturally takes the place it would occupy in the equation, if it were regarded as the electromagnetic mass of the charge e . This is the justification, according to our view, of the term "mass of the charge" for m_0 . But it is free of those limitations which are implied in the derivation of this mass in the usual way by endowing the charge with a structure. Thus l_0 becomes identical with the familiar fundamental length h/m_0c described as the Compton wave-length.

The other fundamental length close to that described in the classical theory as the radius of the electron arises at once from equation (14) since we have

$$\alpha e = e^2/m_0 c^2.$$

Although it does not contain h , it emerges from the principles of the quantum theory. On this point we are in disagreement with Born, who holds that the problem of introducing the so-called radius of the electron, and the difficulties associated with electron-structure have nothing to do with the quantum theory⁽⁵⁾. Equation (14) makes it possible to describe the path of the charge e by means of a null geodesic. We may therefore regard an electron, a positron (which is simply an electron with its fifth component of momentum reversed) and a photon as different aspects of the same thing.

We have to account for the fact that the electron appears to possess a property which has hitherto been described by giving it a radius. The question is, what is the meaning of this from our point of view? It has been shown that both the equation of Schroedinger and that of Dirac⁽⁶⁾, when applied to an electron in an electromagnetic field, can be regarded as gauging equations. That is to say, they suggest that a particular form of gauging is adapted to the description of the physical world.

The form is a modification of that originally suggested by Weyl and generalized by Eddington in order to include electromagnetic phenomena within the theory of relativity. The modification has the advantage that it gives to Weyl's theory the physical content of which it was deprived by his own standpoint with regard to it.

With this view of the nature of the quantum equations in mind, it has recently been shown⁽⁷⁾ that it is impossible to regard two electric charges e as lying closer together than a distance of the order $e^2/m_0 c^2$, which by equation (14) is the same as αe .

It would thus appear that any charge e can be regarded as surrounded by a region of linear dimensions of this order which may be regarded as the exclusive property of the charge, and to distinguish between points lying within this region

would have no meaning. The region is for physics what the point singularity is for mathematics⁽⁸⁾.

This metrical argument introduces the electron radius as a limitation imposed on measurement by a peculiarity of space-time, or at least of our method of space-time description. It has been shown from the same point of view that another limitation exists with regard to measurement along the track of the geodesic which represents the path of the electron. The limitation is that it is not possible to distinguish two points on the path which lie closer together than the length h/m_0c ; this follows from the fact that the geodesic is a null geodesic and that x^5 has only the values nh/m_0c .

Whether these considerations actually justify us in concluding that these two fundamental lengths are of the nature of minima in the physical world or not, is uncertain. But we can at least say that it would be surprising if, with our present methods of description, lengths less than these were to be discovered as significant in any observation.

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OXIDE-COATED CATHODES: I. PARTICLE-SIZE AND THERMIONIC EMISSION

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ABSTRACT. The emission from an oxide cathode increases as the particle-size of the oxide decreases. It is shown that the smaller particles give a more uniform emitting surface and increase the ratio of emitting to non-emitting areas. The size of the oxide particles is determined by the method of preparation of the carbonates. The carbonate particles generally undergo no change of size in the process of conversion to the oxide state, but the method of preparation can cause particle-growth during conversion.

§ 1. INTRODUCTION

THE modern high-efficiency oxide cathode consists of barium and strontium oxides applied to a suitable core metal. The cathode is generally prepared by coating the core metal with a barium-strontium carbonate which is decomposed to the oxide by subsequent heating in vacuo. In previous papers^(1,2) we have shown that the maximum thermionic efficiency is obtained when the oxides are present as a homogeneous solid solution, whose chemical composition can vary from equal parts by weight to equal molecular proportions. A homogeneous solid solution of oxides is invariably obtained if the starting-point in the preparation of the oxides is a homogeneous double carbonate.

The results that we have obtained during recent years with such oxide cathodes have led us to believe that the thermionic efficiency of the double oxide is influenced by the method of preparation and application of the coating to the core metal. We have carried out an investigation into the effect of the method of preparation of the double carbonate on its particle-size, and the effect of the particle-size of the carbonate on the thermionic emission of the resulting oxide coating. In order to understand the results obtained, a knowledge of the physical state and appearance of the final emitting surface was necessary, and for this reason we have used an electron microscope to view the emitting oxide surface.

Although this paper is concerned mainly with the thermionic properties of oxide coatings, brief accounts of the methods of preparation of the double carbonates and the effect of the particle-size on time of decomposition to oxide have been included, because these factors play an important part in ensuring the uniform

results necessary in the successful commercial manufacture of devices using oxide cathodes.

§ 2. EXPERIMENTAL DETAILS

(1) *Method of preparation of the carbonates.* The double carbonate is precipitated by the addition of an equivalent amount of alkali carbonate, such as ammonium or sodium carbonate, to a neutral solution of the nitrates, or by passing carbon dioxide gas into an alkaline nitrates solution. The particular method used has a marked effect on the particle-size of the resultant double carbonate. By varying the nature of the alkaline agent or the precipitating carbonate, we have obtained a number of carbonates with different particle-sizes.

(2) *Method of test.* (a) *Application of the coatings.* The different carbonates were all ball-milled for 24 hours in a suitable organic medium in order to form a spraying suspension. The coatings were then sprayed on to cylindrical nickel cathodes,* 35 mm. in length and of external diameter 1.5 mm., so that the coating weight was 5 mg./cm². This corresponded to a coating thickness of 0.1 mm. and left none of the nickel core visible. The spraying conditions were fixed so that all the sprayed coatings had the same appearance. Sample cathodes were taken from each batch, the coating was removed, and the particle-size was measured under the microscope. X-ray examinations of the coatings were also made to determine their physical state and crystal structure.

(b) *Decomposition time and thermionic emission.* The sprayed coatings were assembled in simple diode valves. The anodes were of nickel mesh, cylindrical in shape, 10 mm. wide and 34 mm. long. A barium-magnesium alloy getter was used, and the diodes were pumped with a three-stage mercury-vapour pump with liquid air. The procedure was as follows. The valve was baked at 400° C. and the anode was out-gassed by high-frequency heating. The cathode was then heated at 950° C.† for 30 sec., and at 1100° C. until decomposed. The time taken for a given coating to decompose was defined as the time taken for a Pirani gauge fitted between the valve and liquid-air trap to fall to a given value of pressure. This is made clear in figure 1, which shows a typical {time, pressure} curve. The time taken for a coating to decompose is given in arbitrary units in table 2, for in practice the actual time will depend on the characteristics of the particular pump used. After decomposition, the valves were gettered and sealed off. Cathodes were then activated by drawing 100 ma. space current with the cathode at 1000° C. Emission-measurements were made after the temperature had been lowered to about 600° C. (The power supplied to the cathode was 1 w./cm².)

(c) *X-ray analysis.* The final state of the oxide was determined by X-ray analysis, by a method described in a previous paper⁽¹⁾. Sample coated cathodes were mounted so that after treatment the cathode could be dropped into an evacuated thin-walled glass tube which was then sealed off. The apparatus is shown in figure 2.

* The percentage composition was as follows: nickel over 99.5, magnesium 0.07, iron 0.15, manganese 0.05.

† All temperatures are brightness temperatures measured at the end of each period, for the thermal emissivity of the coating changes as it decomposes, and the temperature rises at a fixed cathode voltage. The temperatures correspond to cathode wattages of 6.5 w./cm² and 9.0 w./cm² respectively.

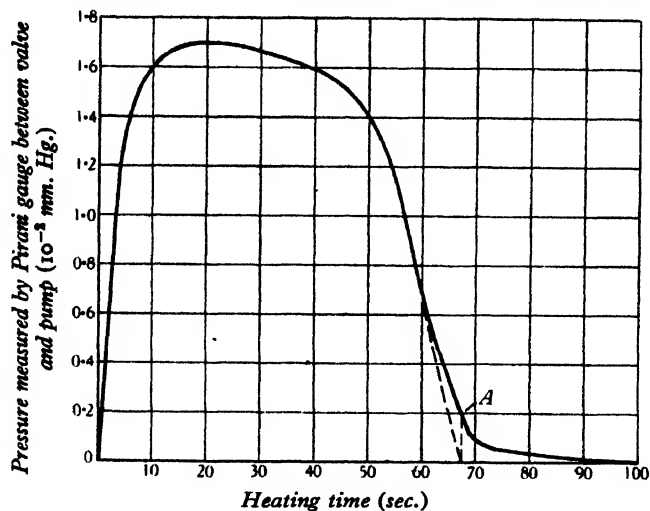


Figure 1. Typical outgassing curve for carbonate coating.

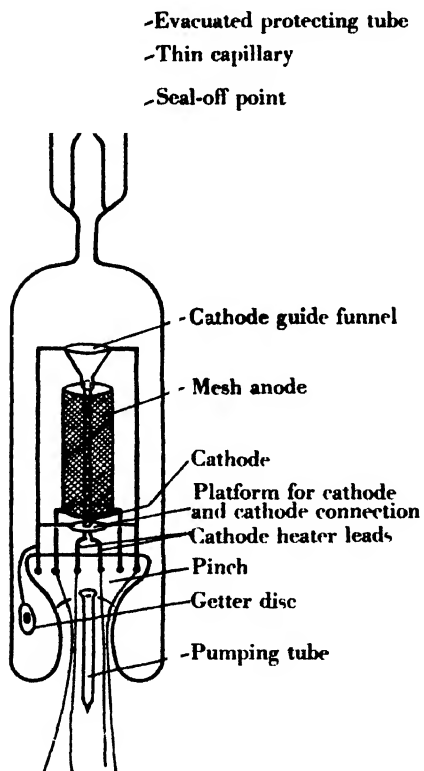


Figure 2. Apparatus for X-ray examination of oxide coating.

§ 3. APPEARANCE OF THE COATING: THE ELECTRON MICROSCOPE

An attempt was made to assess the appearance of the oxide coating after activation. Owing to the rapidity with which the coating changes to hydroxide and carbonate on exposure, it must be examined in a vacuum. The method used for X-ray examination makes this possible, but unless a marked change in appearance has taken place no information about the particle-size of the oxide is obtained. In order to examine the oxide surface in the active condition, an electron microscope was used.

A diagram of the apparatus, which is based on a microscope described by Johansson⁽³⁾, is shown in figure 3. It consists essentially of an electron immersion lens formed by small coaxial apertures in two metal diaphragms placed close together. In the figure, *A* and *B* are two circular copper-nickel plates 0.4 mm. thick, separated from each other by a steatite insulator 1.0 mm. thick. The aperture in *B* is slightly coned, being 1.0 mm. diameter at the front and 1.5 mm. diameter

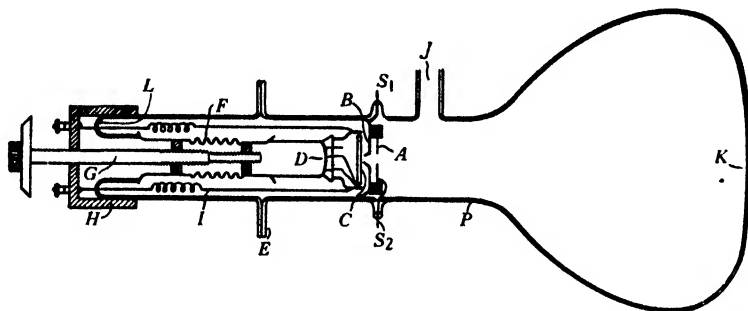


Figure 3. Electron microscope.

at the back. The two diaphragms are supported in the neck of the large bulb *P*, and constitute the electron lens. The cathode core *C* is of nickel, of rectangular cross-section 1.5×2.5 mm., and is 26 mm. in length. It is heated by a *W*-shaped heater wire, and the heater-cathode system is designed so that it makes a push fit on to the supports in the pinch *D*. This arrangement permits rapid interchange of cathodes. The pinch *D* is connected by a glass-to-metal seal to the Tombak bellows *F* and the differential screw arrangement *G*. The pinch end of the system forms a vacuum-tight seal with the main bulb at the ground-glass joint *E*, which has a very large bearing surface. The willemite screen *K*, distant 30 cm. from *A*, is sprayed on the wide portion of the bulb. The whole apparatus is evacuated through the wide bore tubing *J*, which is connected to a three-stage mercury vapour diffusion pump. The leads to the lens are taken out through the walls of the bulb at *S*₁ and *S*₂, and the bulb is internally carbonized from *S*₂ to the screen to avoid bulb charge effects. The carbon surface is connected to the high-voltage lead *S*₂. The heater and cathode leads are taken through the circular seal *L* to the cap *H*. The filament is heated by direct current, so that variable magnetic field effects are avoided. The theory of such a system is dealt with by Brüche and Scherzer⁽⁴⁾. A magnified image

of the cathode surface is thrown on to the screen at *K*. The magnification^{*} depends on the distance of object and image from the lens, and on the ratio of the voltages V_A , V_B applied to *A* and *B* respectively. V_A is approximately 4000 v., and V_B , the focusing voltage, is adjusted to be either slightly positive or slightly negative until a sharply focused image of the cathode surface is obtained on the centre of the screen. The bellows enables the distance of the cathode from the lens to be adjusted, and the cathode is usually set at 0.5 mm. from *B*. The cathode surface can be moved across the lens in either a horizontal or vertical direction by sliding the pinch end of the tube across the joint *E*. The magnification that can be obtained, consistent with sharp focusing, is about $\times 100$.

The microscope is operated in the following manner. The cathode, coated on one flat face with the required coating, is fitted to the pinch, and the ground-glass joint is made vacuum-tight with apiezon L grease. The apparatus is then evacuated, and the pump is operated throughout the time during which the microscope is in use. The cathode is de-gassed and then activated in the ordinary way by drawing space current from it to the plate *B*. The cathode-temperature is then reduced until the emission from the part opposite the aperture is saturated with V_A at about 3000 to 4000 v. This happens at about the normal operating temperature, 750° C., and the image is focused by varying V_B . The image is photographed in the ordinary way. The camera used was of an *F/4.5* double-extension quarter-plate type, orthochromatic plates were used, and the brightness of the image was such that an exposure-time of only a few seconds was necessary.

§ 4. RESULTS

In table 1 we have summarized the different methods of preparation and their effect on the size and shape of the carbonate particles. In figures 4 to 11 are shown ordinary photomicrographs of the particles. The coatings were examined after they had been removed from the sprayed cathodes. In table 2 we have recorded the effect of the particle-size of the sprayed coating on the time of decomposition and the thermionic emission. In the list of carbonates we have included a barium-strontium-calcium triple carbonate and barium-calcium double carbonate. The last two find application in the manufacture of cathodes for special devices such as high-voltage rectifiers operating at high temperatures.

(1) *Method of preparation of carbonates in relation to particle-size.* On reference to table 1, it will be seen that the following conclusions can be drawn. (a) When the carbonates contain barium and strontium (*K* carbonates), or barium, strontium and calcium (*S* carbonates), the particles have a witherite structure. Much finer particles are obtained with the sodium-carbonate method of precipitation than with the ammonium-carbonate method. The ammonium-carbonate method gives irregular aggregates with some spherulites, while the sodium-carbonate method gives mainly needle-shaped particles. (b) When the carbonates contain barium and calcium only (*R* carbonates), the particles have a calcite structure. The sodium-carbonate method of precipitation then gives a slightly larger particle than the ammonium-carbonate method. The particles are also spherulites in each case.

Table Effect of method of preparation on particle-size of carbonates

Nomenclature	Composition (parts by weight)	Method of preparation	X-ray analysis		General particle-size before milling (μ)	General particle-size after milling (μ)	Particle-shape after milling	Speed of addition of precipitant (cm. ² /min.)
			Constitution	Structure				
K_1	Ba, Sr equimolecular	(NH ₄) ₂ CO ₃ added to nitrates solution. Made alkaline with NH ₄ OH	Homogeneous double carbonate	Witherite form	50	50	Large aggregates, mainly spherulites	350 750
K_2	Ba, Sr equimolecular	Na ₂ CO ₃ added to nitrates solution	Homogeneous double carbonate	Witherite form	3	3	Fair number of prismatic needles	350 750
K_3	Ba, Sr equimolecular	CO ₂ passed into nitrates solution. Made alkaline with NH ₄ OH	Generally two phases very close together	Witherite form	15	15	Mainly spherulites	1000
K_4	Ba, Sr equimolecular	CO ₂ passed into nitrates solution. Made alkaline with NaOH	Generally two phases close together	Witherite form	Less than $\frac{1}{2}$	Less than $\frac{1}{2}$	Large number of needles	1000
S_1	Ba 56, Sr 31, Ca 13	(NH ₄) ₂ CO ₃ added to solution of nitrates. Made alkaline with NH ₄ OH	Homogeneous triple carbonate	Witherite form	100	100	Large crystalline aggregates	350 750
S_2	Ba 56, Sr 31, Ca 13	Na ₂ CO ₃ added to nitrates solution. Made alkaline with NaOH	Homogeneous triple carbonate	Witherite form	7	7	Fair number of needles	350 750
R_1	Ca, Ba equimolecular	(NH ₄) ₂ CO ₃ added to nitrates solution. Made alkaline with NH ₄ OH	Homogeneous double carbonate	Calcite form	3	3	Mainly spherulites	350 750
R_2	Ca, Ba equimolecular	Na ₂ CO ₃ added to nitrates solution. Made alkaline with NaOH	Homogeneous double carbonate	Calcite form	10	10	Spherulites	350 750

* The percentage of precipitate varied from 35 to 90° c. without any effect on particle-size

Table 2. Data relating particle-size of carbonates with time of decomposition and thermionic emission

Carbonate	General particle-size after milling (μ)	Figure no.	Time of decomposition (arbitrary units)	Emission at 1 w./cm. ² diode (ma.)	State of final oxides	Appearance of oxide surface
K_1	50	4	100	70	Homogeneous solid solution	Unchanged
K_2	3	5	94	130	Homogeneous solid solution	Unchanged
K_3	15	6	Not tested	Not tested	Not tested	—
K_4	$< \frac{1}{2}$	7	Not tested	40	Homogeneous solid solution	Crystals had obviously grown, and coating had shrunk
S_1	100	8	94	50	Homogeneous triple oxide	Unchanged
S_2	7	9	86	140	Homogeneous triple oxide	Unchanged
R_1	3	10	81	35	Separate phases of equal strength, 80 Ca, 20 Ba; 20 Ca, 80 Ba	Unchanged
R_2	10	11	81	35	Separate phases of equal strength, 80 Ca, 20 Ba; 20 Ca, 80 Ba	Unchanged

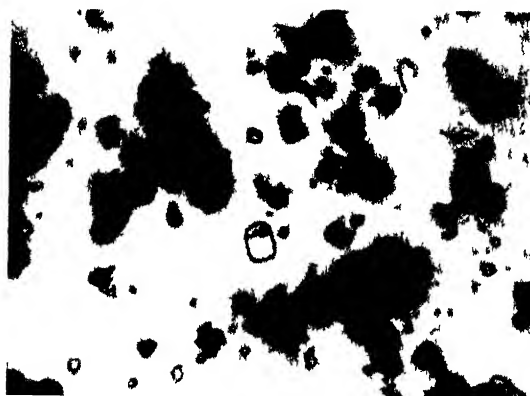
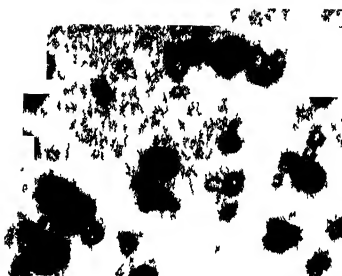
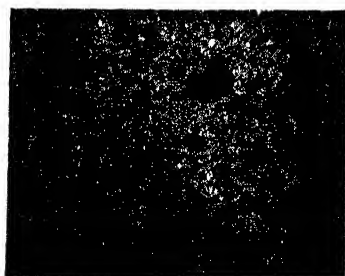
Figure 4 K_1 carbonateFigure 5 K_2 carbonateFigure 6 K_3 carbonateFigure 7 K_4 carbonateFigure 8 S_1 carbonate

Figure 4-8 Photomicrographs of carbonate particles ($\times 500$)

(c) When carbon dioxide is used as the precipitating agent for barium-strontium carbonates, then very fine particles are obtained in the presence of sodium hydroxide, and the particles are mainly needle-shaped. In the presence of ammonium hydroxide the particles are larger, but still smaller than those obtained with ammonium carbonate. Again the particles are mainly spherulites.

In the case of the carbon-dioxide method the rate of precipitation is very slow, and the final product is not a truly homogeneous double carbonate. The two phases are sufficiently close together, however, to have no effect on the thermionic emissions.

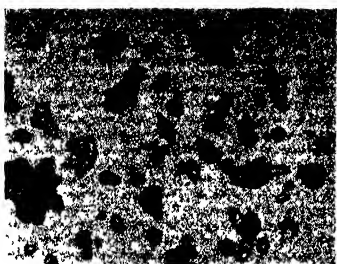


Figure 9. S_2 carbonate.

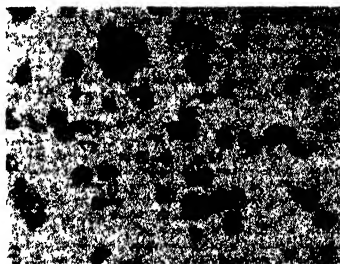


Figure 10. R_1 carbonate.

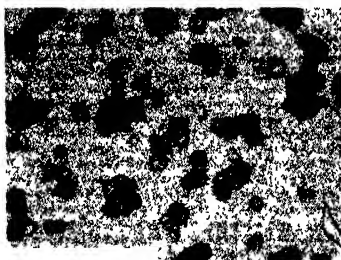


Figure 11. R_2 carbonate.

Figures 9-11. Photomicrographs of carbonate particles. ($\times 500$.)

(2) *Particle-size of carbonates in relation to decomposition time.* On reference to table 2, the following conclusions about the effect of the particle-size of the carbonates on decomposition time and emission can be made. (a) The time of decomposition increases somewhat with increase in particle-size of the carbonate. (b) In each group of coatings a higher thermionic emission is obtained as the particle-size decreases. K_4 at first appears to be an exception, but it was apparent that the final oxide coating had shrunk during the heat treatment on the pump, and this suggested that the particles had probably grown. It may be significant that the finer particles also have the needle type of crystals.

§ 5. PARTICLE-SIZE OF THE OXIDE IN RELATION TO THERMIONIC EMISSION

In figure 12 (*a, b, c*) are shown the electron photomicrographs of K_1 , K_2 and S_1 carbonates. It must be pointed out that the reproductions give no indication of the intensity of the emission, but only indicate the distribution of emission over the surface of the coating. In general, however, the emission-intensity is the same for coatings of the same composition. The size of the emitting spots (white in the figure) is of the same order as the size of the original carbonate particles in each case, and the spots represent the oxide particles on the coating surface. The electron photomicrographs indicate that the differences in thermionic emissions between different coatings can be attributed to some extent to the differences in covering power of particles of different sizes, which give rise to varying emissive areas.

The coating is about 100μ . in thickness, and the particles range from 30 to 100μ ., so that the number of layers present can vary from 30 layers to 1 layer. (In



(*a*) K_1 carbonate sprayed coating. (*b*) K_2 carbonate sprayed coating. (*c*) S_1 sprayed coating.

Figure 12. Electron photomicrographs. Electron image. ($\times 100$.)

actual fact it can be taken that at least two layers were present in the case of the 100μ . particles, for no core was visible.) Since the particles suffer little change in size in passing from the carbonate to the oxide form, it is to be expected that a fine-particle carbonate will give a much smoother surface than a coarse-particle carbonate. It is difficult to measure the actual emitting areas in the photographs, but the ratio between K_1 and K_2 is approximately 3:4. This figure makes no allowance for variations in emission-intensity over any particular particle, and may be compared with the ratio of 1:2 obtained with the diode case at a lower measuring temperature, which is of roughly the same order.

In figure 13 is shown the electron photomicrograph of K_4 coating. It is apparent that the particles are extremely large (about 70μ .) and that therefore the particles, originally $\frac{1}{2}\mu$., have grown considerably in the process of decomposition to oxide. The ratio of the emitting area to that of K_1 is as 5:9, whilst the diode measurements gave 4:7, the agreement again being quite good.

The results indicate that the thermionic emission would be uniformly spread over the oxide surface if the particles were very small. In order to test this view, a

double carbonate was prepared in colloidal form, and its electron image was examined.

§ 6. COLLOIDAL CARBONATE COATING

Patai and Tomaschek^(5,6) have described methods of preparing double carbonates of barium and strontium in colloidal form. The coating is deposited on the core by an electrophoretic method. We have prepared such a coating, and in



Figure 13.

Figure 13. Electron photomicrograph. Electron image $\times 100$. K_1 sprayed coating.

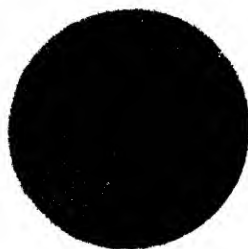


Figure 14.

Figure 14. Electron photomicrograph. Electron image $\times 100$. Colloidal carbonate—applied by electrophoresis.

figure 14 the electron image is shown. It will be seen that the surface is very uniform, a result that fits in with the views expressed above, for the carbonate particles are of the order of 0.1 to 0.02μ , and no growth appears to occur on decomposition. In this connexion Buzágh⁽⁷⁾, in a recent publication, indicates that there is a value of particle-size, just below the upper limit of colloid size, which gives the greatest emission-efficiency.

§ 7. EFFECT OF METHOD OF APPLICATION OF COATING ON THERMIONIC EMISSION

In the experiments described above a given method of spraying the coating on to the core metal was used. Now it is possible to obtain different appearances of the sprayed carbonate, ranging from a powdery appearance to an enamel-like appearance according to the degree of wetness of the spray, which can be controlled by the nature of the diluents used in the spraying suspension. In figure 15 (*a, b*) we show optical photomicrographs which indicate the types of surface that can be obtained. Figure 15 (*a*) shows the typical surface employed in the experiments already described (medium wet spray) and figure 15 (*b*) shows the smooth enamel-like surface that can be obtained with a very wet spray. We have carried out some experiments using a very wet method of application. The suspensions were made up with a large quantity of a diluent which was not readily volatile and it was applied by being painted on to the core metal so that it was running wet. In figure 16 are shown the electron images of K_1 , K_2 and S_1 applied by this method. It will be seen that the K_1 and K_2 images, figure 16 (*a, b*), are similar to those shown in figure 12 (*a, b*), but that the S_1 image, figure 16 (*c*), appears very different from that

shown in figure 12 (c). Its surface appears quite uniform, and as though it were composed of fine particles. This experiment has been repeated a number of times, and in each case a similar result was obtained. The explanation lies in the fact that S_1 differs from K_1 and K_2 in having a very wide spread in particle-size. The particle-size ranges from less than $\frac{1}{2}\mu$. to more than 120μ ., with the greater number of particles

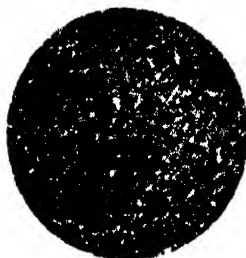
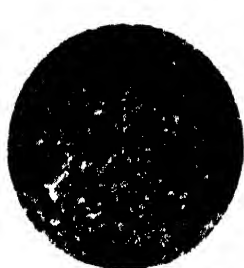


(a) Medium wet spray.



(b) Very wet spray.

Figure 15. Optical photomicrographs of sprayed coatings ($\times 10$)



(a) K_1 carbonate applied wet

(b) K_2 carbonate applied wet

(c) S_1 carbonate applied wet

Figure 16. Electron photomicrographs Electron image ($\times 100$)

at 100μ . A suspension of this nature settles quite rapidly, leaving the finer particles in suspension. In the spray process, where the rate of drying is quite fast, the surface is typical of the particles present in the well-agitated spraying suspension. In the paint process the rate of drying is slow, and the large particles settle rapidly leaving the fine particles in the top surface. The result is important in that it demonstrates that with a carbonate coating where the range of particle-sizes is very large, the method of application may determine to some extent the thermionic results obtained.

§ 8. INTERPRETATION OF THE ELECTRON IMAGE

The work of Brüche⁽⁴⁾ and his collaborators has shown that the electron image is a very good representation of the image that would be seen with an optical microscope. In the photographs we have shown, it has been taken that the emitting spots are images of the oxide particles in the coating surface. It is interesting, however, to inquire into the meaning of the dark patches. Figure 17 shows how a section through the coating would appear. Particles 1 and 3 are on the surface and particles 2 and 4 just below it. Three possible explanations can be suggested for the dark

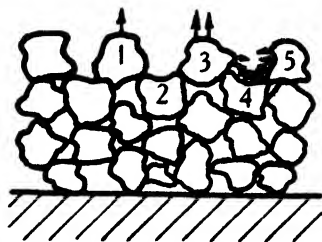


Figure 17. Diagram of section through coating. Core metal.

patches: (1) They may represent gaps in the coating extending down to the relatively non-emitting core, although this is hardly likely to be the case when the particles are of the order of 3μ . in size. (2) They may be images of particles of normal emitting power, which appear non-emitting because of the space-charge effect in the hollows. (3) They may represent particles below the surface which are in fact relatively non-emitting. It is important to know the true explanation, for it may throw some light on the question of the mechanism of the emission. We have devised a series of experiments which deal with the points raised, and we hope to publish the results in the near future.

§ 9. ACKNOWLEDGEMENTS

In conclusion we desire to tender our acknowledgements to the General Electric Company and the Marconiphone Company on whose behalf the work which has led to this publication was done.

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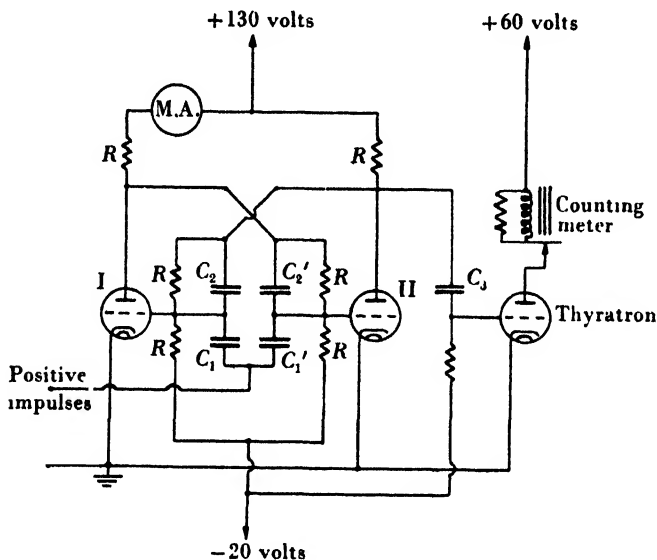
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A SIMPLE SCALE-OF-TWO COUNTER

By HANNES ALFVÉN

Communicated by Prof. M. Siegbahn 14 January 1938. Read in title 11 March 1938

IN a recent paper W. B. Lewis⁽¹⁾ has described a scale-of-two counter using hard vacuum tubes instead of thyratrons. Since about a year ago I have been using a scale-of-two counter which in certain respects is similar to that of Lewis, but as his chokes and cuprous-oxide rectifiers are not necessary in my scheme the latter may be a little simpler. A one-step scale of two of this kind has been used in re-



Valves I and II, Philips B 2038 ($\mu = 33$, $S = 3.5$ ma./v.). All resistances $R = 0.2$ M Ω ; $C_1 = C_1' = 1000$ cm.; $C_2 = C_2' = 500$ cm.; $C_3 = 1000$ cm. For high-speed counting smaller condensers are preferable.

cording cosmic rays at a rate of about 100 impulses per minute, but it can equally well be used in high-speed counting. There are no critical circuit constants, as there are for counters using oscillating valves for example. The counter has worked perfectly with no adjustments at all during several months of continuous counting, for 10^7 impulses.

The circuit is shown in the figure. Just as in Lewis's circuit there are two stable conditions, (1) Valve I is blocked and current flows through valve II; (2) Valve II is blocked and current flows through valve I.

In the first case the plate and grid voltages of the valves are approximately as follows: (I), $V_p = +65$ v., $V_g = -8$ v.; (II), $V_p = +4$ v., $V_g = +1$ v. In the second case the voltages of valve I and valve II are exchanged.

Suppose now that a positive trigger impulse with an amplitude of at least 10 v. arrives, when the counter is in condition (1). As the grid of valve II is positive the grid resistance is rather small, so that the impulse does not change the grid voltage, and consequently does not change the plate voltage of valve II very much. On the other hand, as the grid of valve I is negative the grid resistance is very large, so that the grid voltage increases considerably when the impulse arrives. When the grid voltage reaches about -2 v. plate current starts. Because of that the plate voltage of valve I drops very much, which gives a strong negative impulse through the condenser C_2' to the grid of valve II. When the grid voltage of valve II decreases its plate voltage increases, a positive impulse through condenser C_2 helps the trigger impulse in making the grid of valve I positive, and the counter is brought over into condition (2). The next impulse will in a corresponding way bring it back to condition (1) again.

A milliammeter in one of the plate circuits shows whether the counter is in condition (1) or (2). From one of the plates impulses can be taken to another scale-of-two counter or, as in the figure, to a thyratron with a counting meter. The counter seems to be very stable and reliable. Any of the elements in the circuit can be changed by at least 20 per cent without harm. For example, the permissible latitude of the grid bias was -14 to -28 v.

The circuit can be triggered by negative impulses also, but only if their amplitude is very large. In the cosmic-ray counter the last valve of the amplifier gave negative impulses, and their sign was accordingly reversed by means of a transformer.

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THE PREVENTION OF THE TRANSMISSION OF SOUND ALONG WATER PIPES

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ABSTRACT. Measurements have been made, in the frequency range 50 to 10,000 c./sec., of the transmission of vibration through various lengths and types of rubber hose with a view to determining the value of rubber inserts when used in water systems for reducing the transmission of vibration. The results showed that (1) the insulation obtainable increases with the frequency of the vibration and the length of the rubber pipe; (2) canvas-reinforced rubber is less effective than plain rubber; (3) over the range of diameters tested, the insulation does not vary with the cross-section; and (4) under the conditions of the measurements, sound-transmission through the water contained in the pipe is unimportant.

THE subject of the prevention of sound-transmission along water pipes is assuming greater significance as more and more people decide to reside in hotels or blocks of flats. Noise made in the boiler house, for example, by stoking or, what is probably more important, the pump for circulating hot water, can be transmitted through the hot-water pipes to the radiators and cause a nuisance in rooms remote from the original source of disturbance. Another source of disturbance is the hiss generated by water taps. The water pressure in blocks of flats is frequently quite high, a condition which renders the problem of the hissing of taps and ball cocks very prominent. Sounds of this type are often conducted along the pipes to distant rooms.

The object of this paper is to discuss one method of reducing the transmission of sound by water pipes and to give the results of some experiments made on this subject at the National Physical Laboratory. The method referred to is that of inserting a short length of flexible tubing in the water system, preferably close to the source of noise. This method has been used at the National Physical Laboratory for preventing disturbance in the Acoustics Laboratory arising from the pump circulating hot water. Measurements on this installation⁽¹⁾ have shown that an insulation of some 10 db. against the low frequencies generated by the pump can be obtained by using a flexible insert consisting of a 3-ft. length of rubber hose reinforced with canvas.

The explanation of the insulating action of such rubber inserts is complicated, because transmission along both the pipe and the water column has to be con-

sidered. The insulation against transmission along the walls of the pipe can be calculated⁽²⁾ by using a well-known formula:

$$\begin{aligned} \text{Insulation } R &= \frac{\text{energy of initial vibration}}{\text{energy of vibration transmitted by insert}} \\ &= 1 + \left(\frac{r^2 - 1}{r^2 + 1} \right)^2 \sin^2 kl \end{aligned} \quad \dots\dots(1),$$

where r is the ratio of the specific acoustic resistances of the metal and rubber pipes, including an allowance for their relative cross-sectional areas; $k = \omega/c$, where ω is the pulsance of the sound and c the velocity of sound in rubber; and l is the length of the rubber insert.

As regards the insulation provided by the water column, this may be calculated by a formula given by P. J. Korteweg⁽³⁾ for the velocity of sound in a fluid contained in a pipe with yielding walls. The formula is:

$$\frac{c^2}{c_r^2} = 1 + \frac{2ER}{aE_1(1 - 5a/6R)} \quad \dots\dots(2),$$

where c is the velocity of sound in the free fluid, c_r the velocity of sound in the fluid in the pipe, E the elasticity of the fluid, E_1 the elasticity of the walls of the pipe, R the radius of the tube and a the thickness of the wall of the pipe. By combining this formula with formula (1) the attenuation in the water column can be calculated, and under ordinary conditions it is not likely to be more than a few decibels. Before the sound conducted through the water column can be heard, however, it has to be transmitted from the water to the wall of the pipe and at this stage a further attenuation takes place, the magnitude of which cannot easily be assessed. The existence of this additional attenuation, the difficulty of deciding the relative importance of the pipe and water paths, and doubts regarding the elastic constants of rubber hose, indicated the need for an experimental investigation.

In the measurements described below an attempt was made to determine the insulation obtainable from various lengths of rubber insert. Two types of rubber were used and pipes of several diameters were employed. An attempt was also made to determine the importance of the water path by measuring the insulation with and without the presence of a water column.

The experimental arrangement is shown in figure 1. Two 3-ft. lengths of iron pipe joined by the rubber hose under test were supported horizontally on elastic suspensions as shown, the design being such that the area of contact of the support with the pipe and the stiffness of the elastic insulation of the supports were both as small as possible. This arrangement was adopted in order to minimize the damping of the pipe vibrations. One of the lengths of pipe was driven at the end remote from the rubber hose at a series of warbling frequencies between 50 and 10,000 c./sec. The vibration of both pipes was measured at a series of points along them by an electromagnetic vibration detector⁽⁴⁾. The mean square vibration, which is proportional to the energy of vibration, was calculated for each pipe from the results obtained, and the ratio of the two means was taken as the insulation due to the rubber. Check measurements were made upon a 6-ft. length of pipe uninterrupted

by a rubber insert, to confirm that there was no attenuation along the metal pipe itself.

It must be acknowledged at once that this method of determining the insulation due to the rubber insert can be criticized on the ground that such inserts are usually used in connexion with much greater lengths of metal pipe. This is not, as a matter of fact, always the case; for example, a rubber insert is sometimes used near a tap to prevent the water hiss from being carried back along the pipes. As, however, the use of a considerable length of pipe would have introduced experimental difficulties and would have rendered standardization of conditions troublesome, the method of measurement here described was adopted. It is probable that even if the absolute magnitudes should need modification in the light of future investigation, the relative magnitudes will be found reasonably correct.

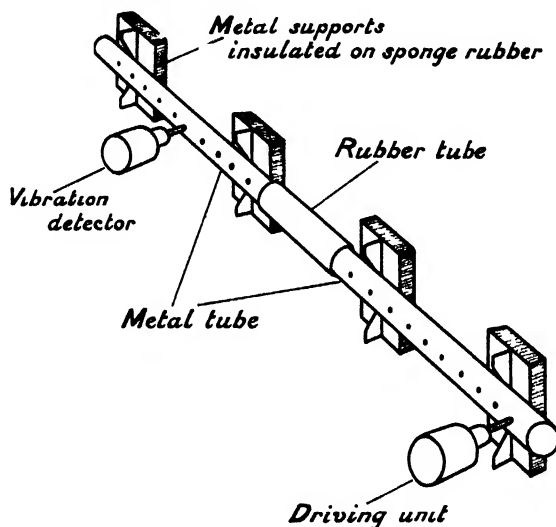


Figure 1. Disposition of apparatus used for measuring the insulation provided by rubber tube inserts.

The results are given in figures 2 to 5, in which the variation of insulation with the length of the rubber is given for a soft red rubber tube and for a black rubber hose reinforced with canvas, respectively. It will be noticed that the insulation is expressed in decibels.* The curves in figures 2 and 3 were obtained by averaging results obtained for two red rubber tubes having walls $\frac{1}{8}$ in. thick and internal diameters of $\frac{3}{4}$ in. and 1 in. respectively. The results obtained with these two tubes were not distinguishable within the limits of experimental error, and the course of averaging them was accordingly adopted. Similarly, the results in figures 4 and 5 were obtained by averaging results obtained with two canvas-reinforced hoses having walls $\frac{3}{16}$ in. thick and internal diameters of 1 in. and $1\frac{1}{2}$ in. respectively. The following general conclusions emerge from the measurements.

* The insulation expressed in decibels is ten times the common logarithm of the ratio of the mean square vibrations in the two pipes.

(1) For a given rubber pipe, the insulation increases with the test frequency up to several thousands of cycles per second and thereafter appears to decrease again. No

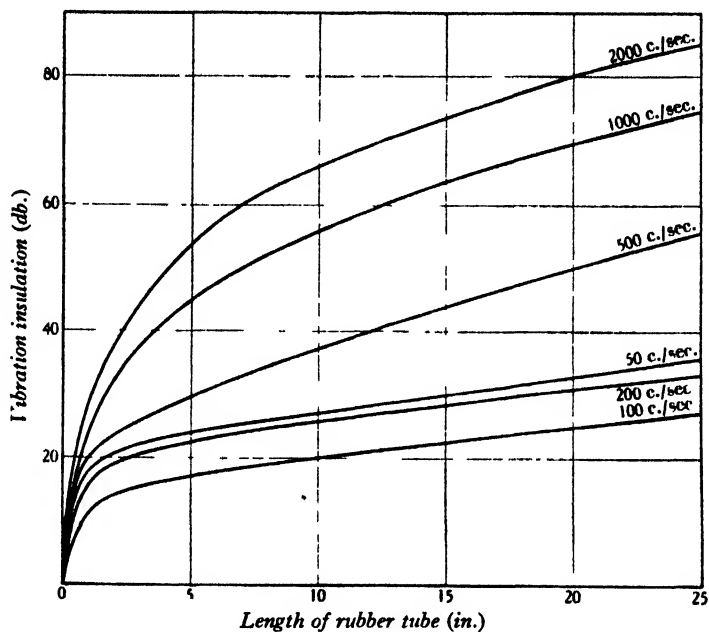


Figure 2. Insulation provided by soft red rubber hose. (Results averaged for tubes having internal diameters of $\frac{3}{4}$ in. and 1 in. respectively.)

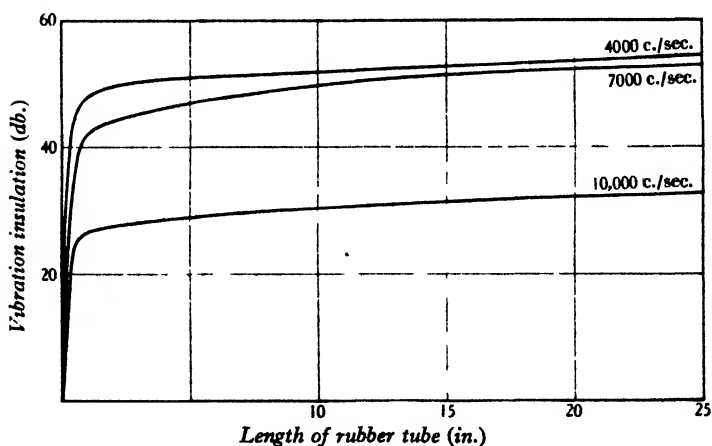


Figure 3. Insulation provided by soft red rubber hose. (Results averaged for tubes having internal diameters of $\frac{3}{4}$ in. and 1 in. respectively.)

satisfactory explanation of this effect was obtained. Tests confirmed that it did not originate in the instruments used for the measurement so that it must, it seems, be ascribed either to a modification in the elastic properties of rubber at high frequencies

or to a change in the mode of sound-transmission through the water or rubber. Actually this frequency region is not important in practice.

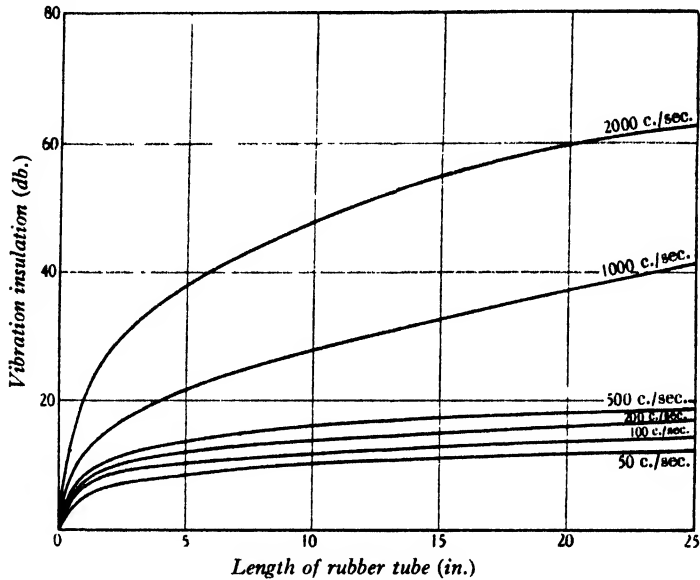


Figure 4. Insulation provided by canvas-reinforced rubber hose. (Results averaged for tubes having internal diameters of 1 in. and $1\frac{1}{2}$ in. respectively.)

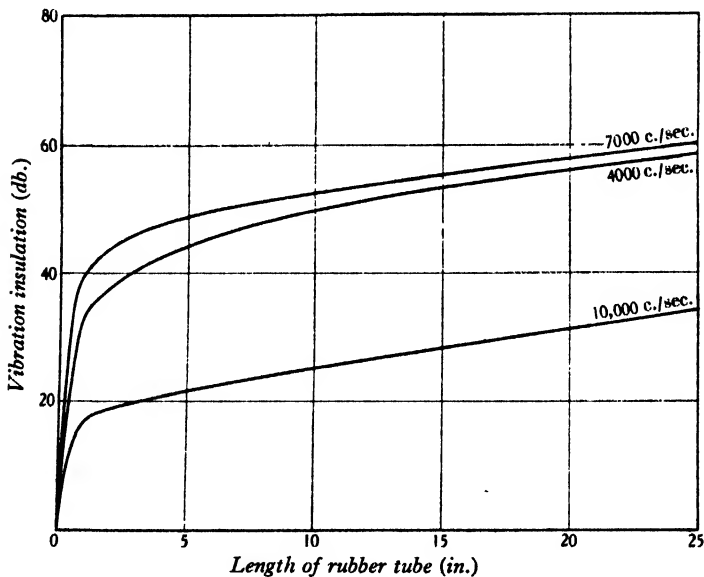


Figure 5. Insulation provided by canvas-reinforced rubber hose. (Results averaged for tubes having internal diameters of 1 in. and $1\frac{1}{2}$ in. respectively.)

(2) At the same test frequency the insulation, on the average, increases as the length of the rubber pipe is increased. There are occasional indications of the

insulation passing through a minimum for certain lengths, but the minima are not well established and could be ascribed as well to resonance effects in the metal pipe as to such effects in the rubber.

(3) Canvas-reinforced rubber, which is stiffer and probably has more internal friction than plain rubber, is not so effective an insulator as the latter. It can, nevertheless, provide quite a reasonable insulation.

(4) Over the range of pipe-diameters tested, insulation does not vary with the cross-section.

(5) Under the conditions of the experiment, conduction through the water column is unimportant, the results being, within the experimental error, independent of whether the pipes contained water nor not.

It will be noticed incidentally that the insulation of 10 db., quoted earlier, obtained from measurements of the attenuation of low-frequency hum by a 3-ft. length of canvas-reinforced hose inserted in a hot-water system agrees with the value which the curves would predict for this length. This result suggests that the curves would be fairly generally applicable to rubber inserts in actual water systems.

The practical significance of these results is that for the greatest insulation a soft rubber is necessary; that for insulation against low-frequency sound a considerable length (of the order of feet) of rubber pipe should be used; and that high frequencies, such as tap hiss, can be dealt with by comparatively short lengths of rubber.

ACKNOWLEDGEMENTS

The author wishes to express his thanks to Dr G. W. C. Kaye, Superintendent of the Physics Department, for his encouragement and to Dr A. H. Davis for criticism and advice. Mr W. C. Copeland rendered valuable assistance in constructing the apparatus and making the measurements.

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DISCUSSION

Dr O. KANTOROWICZ. The author attributes the high insulation value of a rubber hose inserted in a pipe line mainly to the reflection of waves at the boundaries between steel and rubber and between water in the steel tube and water in the rubber hose. Rubber has a high mechanical hysteresis and I think this might play a part, as the energy used by the wave in bulging up the rubber hose, as it travels along the water, will not be delivered back fully. The form of the curves in figures 2 to 5 suggests a mixed mechanism of attenuation. The first steep rise might be due

to reflections as suggested by the author, but the further rise of the insulation must be due to the material in between the reflecting boundaries, and I suggest that it may arise from internal damping in the rubber. It might be possible to reach a decision on this point by using two or more rubber inserts of short length in series, and comparing the {insulation length} curves thus obtained with those published. I do not feel satisfied, however, that the experimental arrangement shown in figure 1 allows of the observation of waves travelling longitudinally, for the transmitter is so set as to put only transverse vibrations into the system, and the receiver is set to pick up only transverse vibrations from the system. I suggest that in this arrangement the pipes with the water as a whole are vibrating transversely, somewhat like strings. This would explain why there is no real difference between full and empty pipes. Filling would merely increase the inertia, thereby lowering both the amplitude for equal energy and the wave-speed along the tube. Neither of these seems to have been measured. At the boundary between rubber and steel, the rubber receiving the same travelling impulse as the steel must move through much bigger amplitudes, as its stiffness and its inertia are so much lower; hence for equal lengths of piping there should be more energy at any time in the rubber than in the steel, and therefore the comparatively high damping capacity of rubber should make itself felt in an accentuated manner.

Dr E. G. RICHARDSON. I am surprised that there is no evidence given by the records of a resonance in the pipe system within the range of frequencies covered. Can the author give us any indication of the natural frequencies of the system sketched in figure 2? It might be possible to work these out on impedance principles, although I suppose that, even if considerably idealized, the system would involve an awkward acoustic circuit of impedances in series and parallel.

Dr R. T. BEATTY. It would be interesting to find out whether the energy was transferred appreciably to the water, or whether the experiment, in effect, dealt with transmission in pipes.

AUTHOR'S REPLY. In reply to Dr Kantorowicz: I doubt whether hysteresis in the rubber is as important as its low elasticity. My reasons are that (1) the attenuations were too high (up to more than 100,000,000, i.e. 80 db.) to be accounted for by hysteresis; (2) canvas-reinforced rubber hose, which presumably has greater hysteresis losses than soft rubber hose, is considerably less insulating, as is shown in the paper. I agree that probably the vibration imparted to the pipe consisted of transverse more than of longitudinal waves, though I think there is no doubt that it is extremely difficult to get one type of vibration without the other. However, in the practical problem of reducing noise from water pipes, transverse waves have the greater importance since they radiate more sound into the air. This was the reason for using the experimental arrangement described.

In reply to Dr Richardson: The resonance of the steel pipes was of the order of thousands of cycles per second. This probably accounts for the apparent loss in insulation of the rubber pipe at frequencies above 4000 c./sec. Calculation of the

resonances of the rubber pipe is difficult owing to uncertainties as to the elastic properties of rubber.

Dr Beatty raises an important point. Possibly one could meet his criticism by driving the water directly by means of a plunger system, and probably an opportunity will present itself for making measurements on these lines. For the present I can only rely upon other measurements (*Engineering*, Nov. 26, 1937) of the insulation provided by a rubber pipe against vibration communicated by a circulating-pump to water in a heating system. The results obtained agreed with the results presented in this paper for a frequency of 100 c./sec. (the frequency of the vibration generated by the pump). There are, of course, theoretical reasons for expecting that conduction of vibration through the water column would be unimportant, namely (1) the fact that such vibration is attenuated by the rubber connexion, (2) the inefficiency of transmission of vibrational energy from water to steel (such transmission has to take place before the sound can be heard), (3) the vibration in the water column must be longitudinal and will on this account be ineffective in generating radial vibration in the steel pipes.

THE TRANSMISSION OF SOUND IN A BUILDING BY INDIRECT PATHS

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ABSTRACT. A description is given of experiments made in a reinforced-concrete building to determine the extent to which sound was transmitted from room to room otherwise than directly through an intervening partition or floor. It is found that operating a loudspeaker in one room generated a sound-intensity in a room 55 ft. away which is not very much less than that in the room next to that containing the loudspeaker. The results show that, in the building considered, indirect transmission between two rooms was comparable with the direct transmission when the intervening partition (in this case a floor) had an insulation of about 50 db. For partitions having a smaller insulation the indirect paths were of less importance.

§1. INTRODUCTION

CONSIDERABLE investigatory work has now been carried out regarding the construction of sound-insulating partitions and a number of the principles which should be followed are now clear^(1, 2, 3, 4, 5, 6). It is obvious, however, that the intervening partition is not the only path by which sound can travel between two rooms. The flanking walls and floors, for example, must also play their part and there must come a stage at which improvements in the sound-insulating value of the partition alone produces very little effect upon the insulation between the rooms.

For the purposes of this paper, paths by which sound travels between two rooms are divided into the direct path through the intervening partition, and indirect paths through the building fabric.

With the object of obtaining an idea as to the importance of the indirect paths, measurements have recently been made in a block of one-room flats and the results are given below. The building concerned was a ten-storey reinforced-concrete building, the outer walls being solid and having an estimated weight of 70 lb./ft.² Internal partitions were double, consisting of two leaves of light 2-in. building blocks with a 2-in. air space between them.

For the purpose of the measurements a loudspeaker generating a warble note was placed in one room and the sound-intensities in that and a number of other rooms in the building were measured. Measurements were also made of the wall vibration in the majority of these rooms. Frequencies of 200, 700 and 2000 c./sec. were used for the measurements. It was found, however, that the background noise was too high for satisfactory measurements to be made in all the rooms at the

upper two frequencies, owing, presumably, to the greater insulating value of partitions at higher frequencies. The results given below are accordingly, except where otherwise stated, for 200 c./sec. only, these measurements being the most accurate. It may be stated, however, that wherever measurements were possible at the higher frequencies, the general conclusions agreed with those obtained from the measurements at 200 c./sec.

§ 2. TRANSMISSION OF SOUND HORIZONTALLY

In the first series of measurements, the sound transmitted in a horizontal direction was determined, the arrangement of the rooms concerned being as shown schematically in figure 1. The results obtained are given in table 1, in which the air-borne sound intensities in the rooms (measured in decibels above an arbitrary

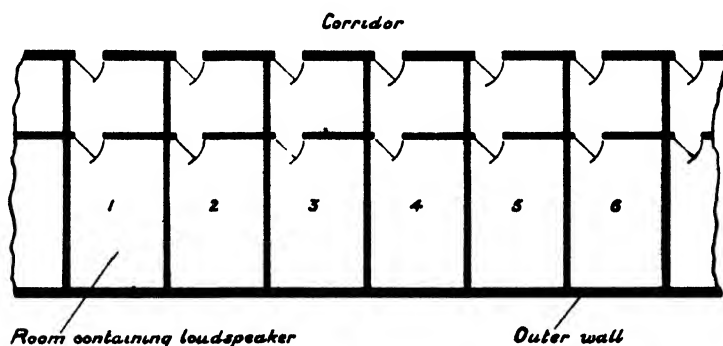


Figure 1.

zero) and the mean vibration of the flanking wall are given. It will be noticed from figure 1 that there was only one continuous flanking wall, and it was the vibration of this that was measured. It was not possible to measure the vibration of the floors or ceilings, but probably, since the building is a monolithic structure, the vibration of the outer wall is representative of that of the floors and ceilings.

Table 1. Transmission of sound horizontally

Room	Approximate distance from centre of room 1 (feet)	Air-borne sound intensity in room (db. above an arbitrary zero)	Mean vibration of flanking wall (db. above an arbitrary zero)
1	—	71	—
2	11	32	53
3	22	24	38
4	33	18	35
5	44	20	34
6	55	18	30

It will be noticed that after room 2 there is only a small drop in sound-intensity as the distance from room 1 increases. This is clearly due to sound-transmission by

indirect paths. Confirmation of this view is given by the fact that, within the limits of experimental error, the air-borne sound intensity is approximately proportional to the vibration of the flanking wall.* It will be noticed incidentally that the rate of attenuation of structure-borne sound in the flanking wall is about $\frac{1}{2}$ db./ft. for the frequency (200 c./sec.) used for the measurement.†

§3. TRANSMISSION OF SOUND VERTICALLY

A second series of measurements was made in the same building upon the transmission of sound in a vertical direction. The arrangement of the rooms concerned is shown schematically in figure 2. The loudspeaker was operated in room 1

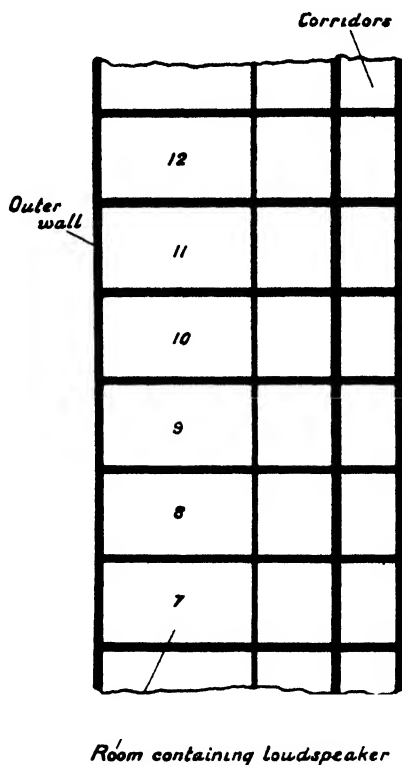


Figure 2.

and measurements of the intensities of the air-borne sound and the wall vibration were made as before. The results obtained are given in table 2. It will be noticed that the decrease of the intensity of air-borne sound with increasing distance is very much the same as for horizontal transmission, considerable sound reaching rooms

* The results are given in decibels and, in consequence, this proportionality is exhibited by the difference between the respective readings being approximately constant.

† A. Gastell⁽⁷⁾ gives a value of 2.5 phon per metre for the attenuation of impact sounds in concrete.

remote from the room containing the loudspeaker. The rate of decay of structure-borne sound in the walls is about $\frac{1}{2}$ db./ft., as for horizontal transmission.

Table 2. Transmission of sound vertically

Room	Approximate distance from centre of room 7 (feet)	Air-borne sound intensity in room (db. above an arbitrary zero)	Mean vibration of flanking wall (db. above an arbitrary zero)
7	—	75	—
8	9	29	44
9	18	27	45
10	27	21	34
11	36	24	33
12	45	18	28

§4. COMPARISON OF HORIZONTAL WITH VERTICAL TRANSMISSION

On comparison of tables 1 and 2 it is noticeable that whereas for vertical transmission, table 2, the sound-intensities in rooms 8 and 9, next and next-but-one to the room containing the loudspeaker, are very similar, when horizontal transmission is considered, table 1, there is a considerable difference between the intensities of the sound in the corresponding rooms, rooms 2 and 3. This suggests that, as regards sound-transmission between two rooms in a vertical direction, the indirect paths are

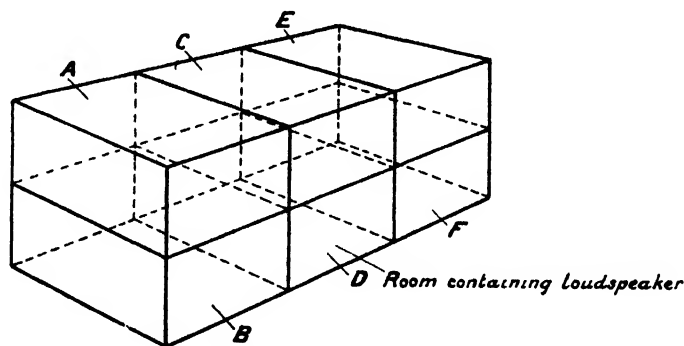


Figure 3.

comparable with the direct path through the intervening floor. On the other hand, in the case of horizontal sound-transmission, the direct path through the partitions was definitely more important than the indirect path. In fact, an improvement in the sound-insulating properties of the partitions could usefully be made, but an improvement in the insulation provided by the floor against air-borne sound would have little value.

To obtain another value for the sound transmitted by indirect paths, measurements were made in a group of six rooms situated as shown in figure 3. With the loudspeaker situated in room *D*, measurements were made of the intensities of air-borne sound in rooms *A*, *B*, *C*, *E* and *F*. As is shown in the diagram, sound will

reach rooms *A* and *E* by indirect paths only. The indirect paths are in this case somewhat different from the indirect paths which exist during horizontal transmission, in that there is only one common floor in the case of diagonal transmission. The other common floor is, however, replaced by the common vertical partition. The contributions by these paths are probably about the same as they would be if the rooms had been adjacent and on the same level. The results obtained are given in table 3, in which is shown the mean sound-insulation against sound transmitted in horizontal, vertical and diagonal directions.

Table 3. Comparison of horizontal, vertical and diagonal transmission for a set of six rooms

Frequency (c./sec.)	Mean insulation against sound transmission (db.)		
	Horizontally	Vertically	Diagonally
200	41	44	49
700	41	49	49
2000	56	56	> 56

§5. GENERAL CONCLUSIONS

When these results are averaged it appears that, in the reinforced-concrete building studied, the sound transmitted by indirect paths was not of great importance as far as horizontal transmission was concerned, but was appreciable for vertical transmission, the difference arising from the fact that the floors were on the average 6 db. better sound insulators than the partitions. In other words, there would be an advantage in increasing the insulation of the partitions from their present mean value of 44 db. up to about 50 db., but no increase beyond this point would be of any value unless some attention was paid to indirect paths of sound transmission.

As regards the possibility of predicting the magnitude of the indirect transmission, it is early yet to attempt any generalization. It is significant that the mean insulation against indirect transmission was about 50 db. in the building studied, a figure which is the same as the insulation that would be expected from the flanking walls and floors (each weighing 50 to 70 lb./ft²) if used as partitions between two rooms. That is to say that it seems, at least in the case of monolithic concrete structures, that the vibration acquired by a wall or floor when air-borne sound falls upon it can be transmitted with little attenuation, along the length of the wall, to neighbouring rooms.

§6. ACKNOWLEDGEMENTS

The author wishes to express his thanks to Dr G. W. C. Kaye, Superintendent of the Physics Department, for his encouragement and to Dr A. H. Davis for criticism and advice. Mr R. Berry rendered valuable assistance in setting up the apparatus and making the measurements.

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DISCUSSION

Dr R. SAMUEL. Would it be possible to remeasure the same building after a year or two, in view of the fact that concrete changes its inner (chemical or crystal) structure after that time?

AUTHOR'S REPLY: There is evidence that the sound-transmitting properties of building structures change in the first few weeks. There would be some interest in measuring them again after a year or so, but unfortunately this is rarely possible since measurements such as those described in the paper can only be made when the buildings are unoccupied.

THE ELECTRICAL REPRODUCTION OF IMAGES BY THE PHOTOCONDUCTIVE EFFECT

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ABSTRACT. It was recognized in the early days of television that a modified form of cathode-ray oscillograph might be used as a transmitting device, the electron beam serving as a means for exploring rapidly the image to be transmitted. A. A. Campbell Swinton⁽¹⁾ was amongst those who foresaw this future use of the cathode-ray tube and he attempted, though unsuccessfully, to produce a transmitting tube by replacing the fluorescent screen by a layer of light-sensitive selenium⁽²⁾. Several variations have been suggested in patents⁽³⁾ but no successful television transmitter using the photoconductive effect has appeared. The present paper describes some investigations into this method of producing picture signals, in which a number of light-sensitive materials were examined.* During its preparation two accounts have appeared in which the same method of signal-production has been investigated and results of a similar nature have been observed^(4, 5).

§ 1. PHOTOCONDUCTIVITY

A LARGE number of inorganic solids have been found to possess photoconductive properties similar to those first observed in layers of suitably annealed selenium. The processes involved are very complicated, but the work of Gudden and Pohl⁽⁷⁾, who investigated the effect in single crystals has contributed to a clearer understanding of the effect. They classified two types of crystal, those (idiochromatic crystals) which give a photoelectric conductivity immediately on illumination in the normal state, and those (allochromatic crystals) which only do so as a result of the introduction of foreign atoms or particles into the crystal lattice by certain external agencies. The former are crystals of high refractive index, and include sulphides and oxides of many heavy metals and some crystalline modifications of some pure elements⁽⁷⁾. This paper is concerned with the investigation of materials entirely of this class.

The current observed to flow under illumination was separated by Gudden and Pohl into two components, the primary photoelectric current, and the secondary current. The primary current corresponds to the actual internal photoelectric phenomenon and can be separated in certain crystals into (a) the negative primary current, which is the liberation of the electrons by the light and the motion of

* A demonstration of the use of the photoconductive effect in a television transmitting tube, based on the work here described, was shown at the Television Exhibition at the Science Museum in South Kensington from June to September, 1937.

these electrons through the crystal lattice, and (b) the positive primary current which is the supplementation of these electrons in order to neutralize the space charge formed by such excitation.

The passage of the primary current may produce a change in the lattice and cause a decrease in resistance, thus giving rise to a secondary current. This differs in several respects from the primary current. It does not, for instance, follow the changes of light-intensity without delay. It does not vary linearly with the light-intensity, and it may be several times bigger than the primary current, which approaches a value equivalent to the number of absorbed light quanta. Secondary currents predominate in cases where there are many centres of disturbance in the lattice, so that since most of the work to be described was done with polycrystalline powders, it appears probable that secondary currents are the effective ones.

§ 2. EXPERIMENTAL METHOD

The materials for testing were deposited as a layer on a conducting metallic base, the signal plate *M*, figure 1, and mounted in an envelope *E* which could be evacuated. In some cases a transparent metal layer was used as the signal plate to allow illumination of the test layer from either side. Also mounted in the envelope was a simple type of electron gun *G* which produced a cathode-ray beam to scan the test surface with a pattern of about 200 lines 50 times per sec. The accelerating

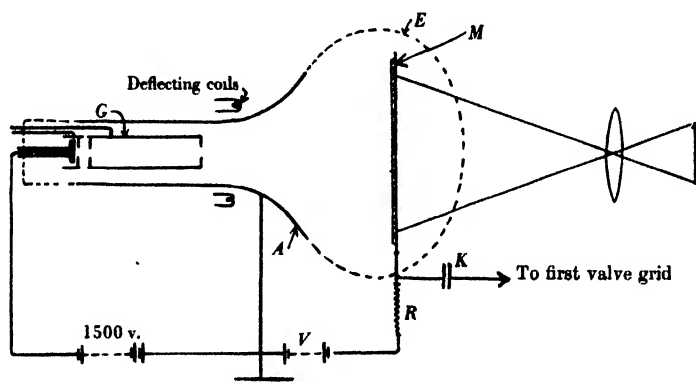


Figure 1. Experimental arrangement of test apparatus.

potential used was 1500 v. The secondary electrons emitted from the layer were collected on an anode *A* on the walls of the envelope. The signal plate was connected to earth by a resistance *R* of about 1 megohm and a battery *V* which supplied the potential necessary for the collecting of the secondary electrons. The current passing through the layer caused a potential-drop across the resistance, the signal plate end of which was connected through a condenser *K* to an amplifier. The output of this amplifier was used to modulate the beam in a normal cathode-ray receiver tube scanned synchronously with the tube containing the materials under test. As the scanning beam passed from illuminated elements to unilluminated ones

the changed resistance caused the current down the signal-generating resistance R to be modulated, and a picture signal appeared on the receiving tube.

Many materials were tested in a vacuum tube pumped continuously, the plate M in this case being sealed on to the end of the envelope with Apiezon sealing compound Q , and being easily removable. In other cases the materials were tested in sealed-off tubes after a rigorous baking treatment.

The materials in general were prepared for testing by a chemical precipitation process followed by heating in nitrogen to about 900°C . A long grinding in a ball mill followed, after which the layer was produced from the fine aqueous suspension either by spraying or settling on to the metal plate. Some materials required special treatment, and for these cases notes on the preparation are given in table 1 which presents the general results.

§ 3. RESULTS OF EXPERIMENTS

By the method described a large number of materials were tested, some being known photoconductors and others those which might be expected to show such an effect. They are listed in table 1, and the form in which each was tested is noted.

In many cases definite signals were observed when a strongly illuminated pattern was projected on to the test layer. It was found that if the anode A was held at a potential in the neighbourhood of M , or even negative to M , in general weak signals were obtained in such a direction that increase of illumination caused negative potential pulses on the signal plate. With an amplifier having an even number of stages, therefore, a bright spot on the layer appeared as a dark spot on the received picture. Such signals will be called negative signals. When the anode was made increasingly positive with respect to M , so that secondary electrons were collected, the signals were found to disappear for a certain voltage between about $+10\text{ v.}$ and $+30\text{ v.}$, the actual value depending on the geometry of the tube. With further increase in V the signals reappeared and were of the opposite sign, i.e. increasing illumination caused positive potential pulses on the signal plate. They increased in magnitude with increasing V up to about $V=50\text{ v.}$, and in some cases passed through a maximum value.

The strong signals were found in most cases not to disappear instantaneously on cutting off the light but to die down gradually in a time amounting to several seconds. This lag was not interpreted as being wholly due to the known lag of the photoconductive effect but was attributed to the comparative slowness of the potential-changes which were produced by scanning, in a manner to be explained later.

The last column of table 1 contains notes on the observed behaviour of the tested materials. Of these, zinc selenide proved to be the most sensitive, and on it most observations were made. More detailed results will be described and the mechanism of the production of signals will be discussed with special reference to this material. The region of the spectrum which produced the observed signals

was found approximately by the direct use of colour filters in the incident light beam, and the results are noted in column 3.

Table 1

Material	Preparation for testing	Observations
Selenium	Layer deposited by evaporation in vacuum followed by annealing at 180° C. in air	Very faint signals observed for small + or - values of V . Sensitive to yellow-orange region of the spectrum
Zinc sulphide	Standard fluorescent preparations used	Strong signals observed in ZnS, ZnS-Cu, ZnS-Mn, ZnS.CdS.-Cu but not in ZnS unheated.* Sensitive in blue-violet range
Cadmium sulphide	Normal preparation	Signals produced by red-yellow region of spectrum
Thallium sulphide	(1) Precipitated and deposited as sprayed layer without oxidation (2) Layer oxidized by heating in air†	No signals Faint signals obtained with little lag and produced by far-red and infra-red light
Antimony sulphide	(1) Precipitated red crystalline form heated in nitrogen at 200° C. (2) Naturally occurring mineral antimonite	Fairly strong signals produced by far-red and infra-red light Faint trace of signal obtained
Zinc selenide	(1) By direct combination of elements (2) By precipitation	Most sensitive material tested. Sensitivity mainly due to yellow region of spectrum
Cadmium selenide	Normal preparation heating, in nitrogen to 700° C.	Faint signals obtained due to red and infra-red light
Zinc telluride	Direct combination of elements	Trace of signals obtained

* Zinc sulphide unheated has no fluorescent properties. "ZnS-Cu" etc. refer to zinc sulphide activated by trace of copper etc. to produce fluorescence.

† As in the commercial Thalofide cell.

The following materials were tested but gave negative results. (1) Silver sulphide prepared both by precipitation with subsequent heating to 500° C. in nitrogen, and by the direct action of hydrogen sulphide on silver. (2) Cupric sulphide, cupric selenide, silver selenide, cuprous iodide prepared by normal precipitation followed by heating. (3) Silver chloride prepared on silver electrolytically. (4) Aluminium oxide prepared by anodic oxidation. (5) Cadmium oxide from the heated carbonate and antimony oxide sublimed from the commercial product. (6) Zinc orthosilicate (willemite) and calcium tungstate, i.e. standard fluorescent preparations. (7) Galena, molybdenite, bornite, copper pyrites, i.e. naturally occurring rectifier crystals.

The oxides of copper were tested in various forms and signals were obtained whose general characteristics differed from those obtained with all the other materials tested.

Cuprous oxide. (1) This substance was prepared as a layer on a copper base by roasting in air and afterwards dissolving off the top layer of cupric oxide. No

signals were obtained until the layer had received some special treatment, such as being subjected to heavy bombardment with a cathode-ray beam, or had received a sputtered layer on its surface in a hydrogen discharge. Signals were then obtained which were positive over the whole range of V , fairly strong and quite free from lag. (2) The cuprous oxide crystals removed from such a plate and sprayed after grinding gave no signals. (3) A sprayed layer of crystals precipitated from cupric sulphate gave no signals though weak signals appeared after heavy bombardment with a cathode-ray beam.

Cupric oxide. (1) This was formed on the surface of a cuprous oxide layer by roasting. Weak signals were observed, opposite in sign to those in zinc selenide and free from lag. (2) The same substance was prepared by heating carbonate at 1000°C . This also gave faint signals.

§ 4. ZINC SELENIDE

(a) *Method of preparation.* The method of preparing zinc selenide by direct combination of the elements has the advantage that hydrogen selenide with its unpleasant physiological properties is avoided. It is however unsatisfactory as very little control is possible, and for accurate working it was necessary to adopt the method of precipitation.

The hydrogen selenide was prepared by the action of water on aluminium selenide and passed into a solution of zinc ammonium chloride which had been highly purified to eliminate heavy metals and other impurities. When an excess of hydrogen selenide was present the zinc selenide was filtered off, washed thoroughly, and dried at 110°C . It was then ground to a fine powder and heated in a tube furnace in an atmosphere of nitrogen to 900°C . For test purposes the resulting product was ground in a ball mill in aqueous suspension for 3 hr., and then sprayed or settled in the manner mentioned above.

The effect of the presence of traces of copper and silver was tested by the addition of 0.01 per cent of these metals to the selenide. Little effect on the photoconductive properties was observed.

The effect of temperature of *activation*, as the heating process is called in fluorescence work, was tested over the range 110 to 1100°C . The material heated at 110°C . gave only very faint signals, but good signals differing little in strength were obtained over the range 500 to 900°C . A decrease in efficiency for temperatures over 1000°C . was observed, which may be due to an increase of particle-size in the test layer, since the material was more resistant to grinding.

In order to produce a sufficiently fine material for settling, long grinding was necessary and tests were made of the stability of the photoconductive properties of zinc selenide under this treatment. Samples were ground for periods up to 50 hr. but little decrease in the photoconductivity was observed. Under settling conditions the reactivity of the selenide with the metal base proved troublesome, but the use of gold-plated signal plates prevented such disturbance.

Despite the attempts to obtain reproducible results there was at first a large

amount of unexplained variation. It seems probable that this was due* to the instability of the selenium compounds during the precipitation process. Three comparison preparations were made to test this supposition. In the first the precipitation was carried through in an enclosed apparatus from which the air had been expelled with nitrogen and then after the precipitate had been filtered and washed rapidly, it was dried in a vacuum desiccator. The second precipitate was filtered and washed slowly and dried at 110°C . in air. The third precipitate was allowed to stand for 2 days and then treated like the second. The colours of the dried materials were respectively pale yellow, pink, and dark red, owing to the presence of varying quantities of free selenium. All were then heated to 900°C ., ground in a ball mill, and tested. The sensitivities of the three samples were in the ratio 1 : 10 : 20. Another test was made, the free selenium being washed out from the last material with sodium cyanide, while the zinc selenide was left as a white precipitate. This after standard treatment gave only very weak signals.

From these results it appears that the presence of free selenium during the activation process plays an important part in the development of the photoconductive properties of zinc selenide. The exact function of the selenium is not clear. No free selenium was detected in the final product by analytical methods, and it is improbable that any was left after the activation process. This view is supported by the observation that zinc selenide gave good signals even after evaporation in a high vacuum had occurred.

(b) *Experimental observations on zinc selenide.* The following observations were made on the signals obtained from zinc selenide. (1) For values of V in the range -200 v. to about $+10\text{ v.}$ negative signals were obtained with a maximum value at about $V=0$. Above this was a short range in which no signals appeared, while from about $+20\text{ v.}$ to $+200\text{ v.}$ strong positive signals were obtained. These were greatest at about $+50\text{ v.}$, being then 10 times larger than the best negative ones obtained with small values of V . (2) For a given value of V the signal is proportional to the current in the scanning beam. (3) The signals did not reach their maximum value immediately on the illumination of the test layer, and on the switching off of the light they disappeared only gradually. This lag phenomenon was negligibly small when V was small or negative, but became very pronounced when V became increasingly positive and attained a value of several seconds when V was $+50\text{ v.}$ The lag decreased continuously with increase in the scanning-beam currents up to at least $10\mu\text{a}$. (4) The relation between signal-size and illumination showed a departure from linearity as the illumination increased and a saturation effect for values of the illumination of about 70 ft.-candles on the test layer. (5) The optimum thickness of the test layer was found to be approximately 2 to 3μ . For greater thickness the light penetrates only a portion of the layer, the rest retaining its high dark resistance. The reduction in sensitivity for smaller thicknesses was due apparently to the fact that owing to the finite particle-size, thinner settled layers were not completely covered. The absorption of light in a wedge-shaped evaporated layer was observed. It appeared that the most sensitive region of the spectrum lay on the long-wave end of the absorption band (a usual property of

idiochromatic crystals) and that the depth of penetration was about 2μ . Layers of the selenide evaporated in high vacuum from a tungsten spiral were found to give strong signals if the thickness was of this order. The signals disappeared for large values of V and had a longer lag than had those observed in the settled layer. It may be noted that for layers of this thickness the distance between the centres of adjacent picture elements during scanning with 200 lines of width 0.3 mm. is large compared to the distance through the layer. On this basis the resistance of the single element is in later sections deduced after the resistance along the layer has been neglected. In practice the pictures obtained were very sharp, the conductivity along the surface being negligibly small.

§ 5. MECHANISM OF SIGNAL-PRODUCTION OF ZINC SELENIDE

A consideration of the behaviour of a highly resistive layer under bombardment by a cathode-ray beam together with a recognition of its photoconductive property gives a satisfactory explanation of the above observations.

As the cathode-ray beam passes over the layer its front surface takes up a potential at which there is equilibrium between the number of electrons arriving in the beam, the number lost to the collecting electrodes as secondaries, and the number passing through the layer to the signal plate. If the resistance through the layer is high, the potential of the front surface is practically that which causes the surface to lose to the collecting anode one secondary electron per primary arriving. The secondary emission from the selenide due to electrons having an energy of 1500 v. has been measured by a ballistic method, and the ratio of secondary to primary electrons is about 2 : 1. An insulated surface of such a low secondary emission would, if bombarded, take up an equilibrium potential several volts negative with respect to the collecting electrode. This potential is the value of V for which no current flows through the signal plate lead, and was found, in the geometrical arrangements used, to be between 10 and 20 v. This was also the value of V for which no signals were obtained.

For other values of V a potential-difference will exist across the layer, and in the intervals between successive passages of the electron beam the potential on the front of the layer will approach that of the signal plate. The rate of leakage will depend on the resistance and capacity of the layer.

The specific resistance of the selenide was estimated by the following method. If potential differences exist over the surface of the layer when it is scanned by the beam, picture signals are obtained, since the loss of secondary electrons to the anode is not constant and varying charges are induced on the signal plate through the elementary capacity. The layer was, therefore, scanned in the dark with a potential-difference V of +50 v. between anode and signal plate. The front of the layer was then charged up uniformly until a potential-difference of perhaps 40 v. existed between the front and the back of the layer. The scanning beam was then cut off and a brightly illuminated pattern was projected for a short time on to the layer. The illuminated parts leaked away rapidly to the signal-plate potential,

deduced simply from observations on the collection of secondary electrons under steady bombardment and under various applied collecting potentials.

The loss in charge from the element initially at voltage v below the collector, due to leakage between successive scans, will be given by an expression of the form

$$\begin{aligned} q' &= Q_0 - Q = Q_0 - Q_0 e^{-t/CR} \\ &= C(V-v)(1 - e^{-t/CR}) \\ &= \frac{t}{R}(V-v) \text{ approximately.} \end{aligned}$$

Here t is the time between two successive scans, Q_0 is the initial charge on the element given by $C(V-v)$, since $(V-v)$ is the initial potential-drop across the layer. CR is the time constant of the decay of charge on the leaky condenser by which each element is represented. Thus

$$q' = k(V-v) \quad \dots\dots(1),$$

where, for a given element, k is a constant inversely proportional to the resistance of the element. To find the value of q for the equilibrium case, in which the charge gained per impact of the beam equals that lost between scans, equation (1) is plotted as the line ST in figure 2, the ordinate of the point of intersection T giving the charge lost and replaced in each complete frame period. The graph of equation (1) crosses the v -axis where $V=v$, so that for different potentials of the collecting anode relative to the signal plate the point S will have varying positions along Ov . S_1T_1 will represent the line for the case in which, say, $V=60$ v., and S_2T_2 will do so for the case in which $V=5$ v. The slope of the line is inversely proportional to the resistance of the element; that is, it is proportional to the illumination. ST , ST' represent the graph of equation (1) under two conditions of low and high illumination for example.

For an element in the dark the slope of the line ST is so small that the point T is always very close to P , whatever the value of V . The ordinate of the point T for an illuminated element, therefore, will be proportional to the signal obtained from that element.

From figure 2 we can thus deduce the following conclusions which agree with the experimental observations. (1) No signals will be obtained if V has a value at which the number of secondary electrons collected equals the number of primary electrons in the scanning beam (that is, if S and P coincide). (2) For increasingly positive values of V the signal-size will increase to a certain maximum in the positive direction. (3) For values of V below P the signals will become negative, since the surface now loses charge on being scanned. The reason for the fact that strong negative signals are not obtained and for the fact that they do not increase with decreasing V is probably that the electrons spread on to the brightly illuminated parts, which are in this case positive with respect to the dark parts. The signal plate becomes positive with respect to the front of the layer in this region, and catches electrons through cracks and at the edges, and again causes a reduction of signal. (4) Increase of illumination causes the point T to move along towards R

even if the potential V is held constant. Satisfactory reproduction of half tones in the picture will be obtained, therefore, only if T is on the sloping part of the curve. There is a flattening off in the signal illumination curve for illuminations above about 60 ft.-candles if $V = 50$ v., and at lower illuminations if V is greater than this.

The incidence of lag also is explained by this mechanism. When the light is first switched on, the signal obtained will grow in intensity until the potential on the front of the layer has been reduced from its dark value to its value for a light element. The time for this will be small if V has a value near to the potential for zero signal, but big if V is big, when $V = 50$ v. it can be expected to be an appreciable fraction of a second.

After the light is switched off, even if the resistance instantly returns to its dark value, a signal will be obtained until the beam has charged up the element so that there is no appreciable difference between its potential and that of an element previously unilluminated.

This also increases with increasing values of V , being negligible for small values. If V is about 50 v. the change of potential produced by the impact of a scanning beam of $1 \mu\text{a.}$ under steady conditions on an illuminated element is only of the order of 0.1 v., but in order to charge up the layer to its dark steady condition a potential-change of possibly 10 v. is necessary, and the signal will, therefore, be observed for 50 or 100 scans after the light has been turned off. In order that the tube may be effective for television transmission it would be necessary to use a beam current large enough to charge up the layer in only one or two scans. Such currents are enormous compared to those normally used in such devices.

§ 6. BEHAVIOUR OF OTHER MATERIALS

According to the mechanism sketched above it appears that if signals are to be obtained for the region in which V is large, a certain minimum dark specific resistance of the layer is necessary. If the element-resistance is too small, both dark and light elements will leak sufficiently during a frame-time to cause saturation of the secondary electrons to the collecting anode on the next impact of the scanning beam. No signals due to illumination will then be obtained. If the dark specific resistance of the material is less than about $10^{10} \Omega\text{-cm.}$, no signals will be obtained for values of V above about 50 v. This appears to account for the behaviour of some materials in which the signals disappeared for large values of V , the case of evaporated zinc selenide layers being one example. Even if the specific resistance is smaller than this value, however, the potential-differences between illuminated and dark elements will give rise to signals if V is in the region where the secondary electrons are not saturated. These signals will be weak and of short lag, and no memory can be expected. The signals obtained on annealed layers of selenium had these characteristics and were only about $1/20$ as sensitive as those obtained in the selenide.

It appeared necessary in certain cases to suggest an additional mechanism for the production of signals, notably in the case of the cuprous oxide layers formed by the oxidation of solid copper plates. The low specific resistance of the cuprous

oxide will account for the lack of signals in the untreated state of the layer. The effect of treatment in a sputtering-chamber or by heavy bombardment by cathode rays is believed to be due to the formation of a blocking layer of high resistance on the surface⁽⁸⁾. Under the influence of light, electrons would pass from the cuprous oxide across this blocking layer, causing the front surface to acquire negative charges. Scanning by the electron beam would then restore the elements to some common equilibrium potential more positive than the potential of the light elements. Positive potential pulses would be produced in the signal plate, giving the observed positive signals. It is possible that both the photovoltaic and the normal photoconductive effects are concerned in certain cases, but the main observations appear to be capable of adequate explanation on the lines suggested above.

§ 7. ACKNOWLEDGEMENTS

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DISCUSSION

MR W. H. ALDOUS. Can the authors give any idea of the uniformity to be obtained in the photoconductivity over the surface of a single screen, and whether it compares favourably with the uniformity of emission over a normal photoemissive surface? To what do the authors ascribe the activation of the cuprous oxide under cathode-ray bombardment?

AUTHOR'S REPLY. The background obtained in these transmitting tubes proved to be serious. This background was due not to variations in photoconductivity but to irregularities in the layer, depending on the size of the settled particles, and to chemical action between the selenide and its supporting layer. An evaporated layer of selenide showed a considerable improvement on the settled layer in this respect. The activation of the cuprous-oxide layer under cathode-ray bombardment is presumed to have been due to removal of excess oxygen from the surface layer of the cuprous-oxide crystals.

THE EQUILIBRIUM OF A BALL SUPPORTED BY A VERTICAL AIR-JET

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ABSTRACT. Experiments on the equilibrium of a ball supported by an air-jet are described. The forces acting on the ball are obtained from pressure-distribution curves.

WHEN a light celluloid ball, of the kind used in table-tennis is placed in the stream of air issuing from a vertical jet, the ball is supported at a height of several centimetres above the jet and oscillates slightly both up and down and from side to side about its position of equilibrium. If the jet has been made by drawing down a glass tube it is frequently found that in addition to its oscillatory motion the ball spins rapidly about an approximately horizontal axis. This rotation is not observed when an accurately made brass jet is used and is thus probably due to a lack of symmetry in the glass jets.

The equilibrium of the ball has been studied by measuring the pressure exerted on different parts of the surface of a similar ball held in various positions both on and off the axis of a vertical jet. Three jet-sizes were used, the orifices being cylindrical, 1 cm. in length and of internal diameter 0.18, 0.25 and 0.33 cm. respectively. The jets were threaded to fit on the end of a vertical brass tube which could be moved either vertically or horizontally in a slide and was joined by rubber tubing to a small Cenco compressor. The ball, 3.8 cm. in diameter, was supported above the jet by a horizontal brass tube about 0.2 cm. in external diameter and coaxial with a diameter of the ball to which it was fastened with Durofix. The tube communicated by a small hole with the inside of the ball, which was itself perforated with a small hole lying in the diametral plane normal to the supporting tube. One end of the brass tube was closed and the other was connected by a short length of narrow rubber tubing to the manometers—a simple U-tube and a tilting gauge, both containing xylol. The pressure, above or below atmosphere, measured by the manometers is thus very nearly the same as the pressure exerted by the air stream on the surface of the ball in the region of the hole. By rotating the ball and supporting tube about their common axis the variation of the pressure over the surface could be observed, the position of the hole being read on a circular scale. The supports did not appreciably disturb the flow of air round the ball.

In an experiment with the jet of diameter 0.25 cm. and the compressor running at full speed, a free ball was supported with its centre approximately 13.5 cm. above

the top of the jet. The variation of the pressure over the surface when the ball was in this position is shown in figure 1, in which the circumference of the ball is indicated by the circle and the axis of the jet by the arrow. The excess pressure above atmosphere is measured outwards from the circumference along the radius. Readings of pressure were taken at least every 10° and the experimental points lie extremely close to the smooth curve shown. A positive pressure is experienced by the lower part of the surface of the ball up to the point at which the radius makes

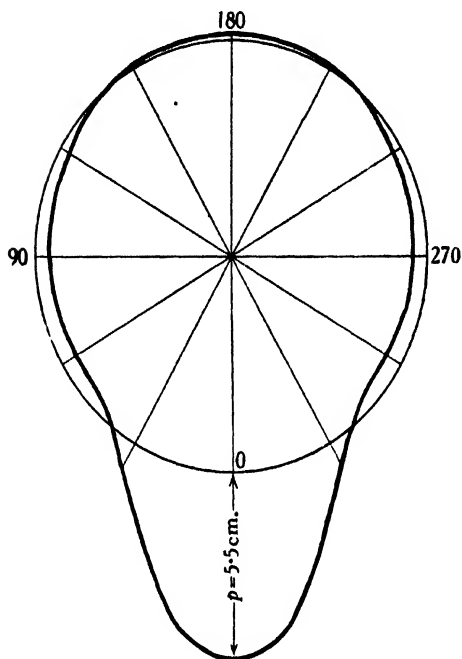


Figure 1. Pressure-distribution with the centre of the ball on the axis and 13.5 cm. above the jet.

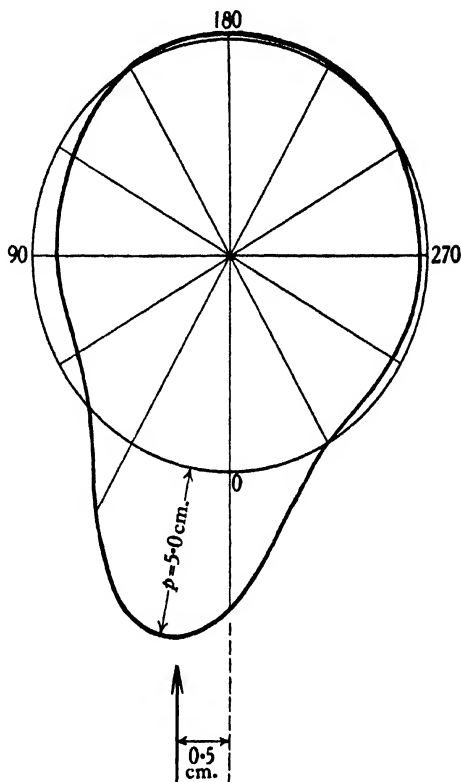


Figure 2. Pressure-distribution with the centre of the ball 0.5 cm. off the axis and 13.5 cm. above the jet.

an angle of approximately 40° with the vertical. From roughly 40 to 140° there is a slight vacuum, while the top of the ball experiences a very small positive pressure of the order of 0.1 cm. of xylol.

The resultant upward force acting on the ball can be determined by graphical integration of the vertical component of the pressure over the whole surface of the sphere. The force obtained in this way is approximately 4.5 g. wt., whereas the weight of the ball is approximately 3.0 g. The agreement is perhaps as good as can be expected. The discrepancy may be largely attributed to the fact that the pressure measurements are probably not accurate to better than 10 per cent in the region from 30 to 180° , whereas this region is extremely important in the calculation

of the resultant force and any error in the measurement of the pressure* is considerably magnified. Moreover, it is possible that the manometer does not give an absolutely accurate measure of the pressure on account of the shape of the hole, although curves obtained with different holes are in quite good agreement. If the distance between the ball and the jet is either increased or decreased the pressure-distribution curves retain the same general appearance, the pressure on the lower part of the ball and therefore the resultant upward force on the ball being greater

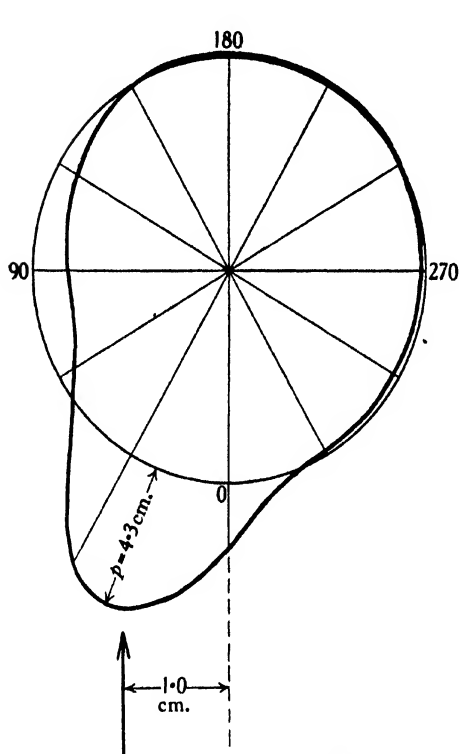


Figure 3. Pressure-distribution with the centre of the ball 1.0 cm. off the axis and 13.5 cm. above the jet.

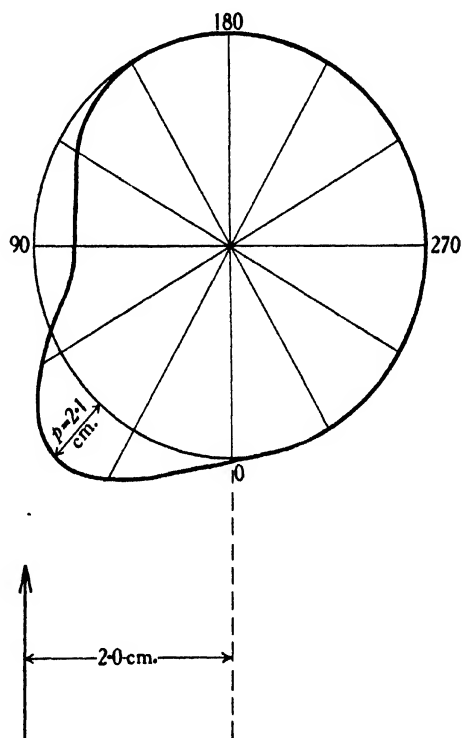


Figure 4. Pressure-distribution with the centre of the ball 2.0 cm. off the axis and 13.5 cm. above the jet.

the less the distance of the ball from the jet. Thus it is clear that a free ball stands at such a height above the jet that the resultant upward force exactly balances the weight of the ball.

The horizontal forces which tend to keep a free ball on the axis of the jet may be studied by obtaining the pressure-distribution curves when the jet is displaced to one side, in the vertical plane through the centre of the ball at right angles to the supporting tube. Curves obtained in this way when the jet is displaced 0.5, 1.0 and 2.0 cm. respectively are shown in figures 2, 3 and 4, the vertical height of the ball above the jet being 13.5 cm. as before. Owing to the unsymmetrical nature of the curves it is not possible to calculate the actual forces acting on the ball. It is quite clear, however, in each case that the side of the ball nearer to the axis of the

jet experiences a greater vacuum than the side farther from the jet, whence there is a horizontal force on the ball which tends to bring it back to its equilibrium position on the axis. Curves are not shown for displacements of the jet greater than 2.0 cm. but a slight vacuum of the order of 0.05 cm. of xylol can still be detected on the near side of the ball when the displacement is as great as 5.0 cm. From the curves it also appears that the resultant upward force on the ball is still considerable when the displacement is 0.5 cm. or even 1.0 cm., but has decreased considerably when the displacement is 2.0 cm. The curves suggest that owing to the reduction in the upward force the ball will fall if displaced by more than about 1.0 cm. from the axis of the jet. Experiments with the other two jets yielded similar pressure-distribution curves.

The above conclusions may be illustrated by a simple experiment in which a light cotton is attached to a ball either by wax or by being knotted through a small hole. If the ball is now supported by the air-jet and the cotton is pulled horizontally by the hand the ball becomes displaced and the horizontal restoring force on it is felt by the hand; but when the displacement exceeds about 1.0 cm. the ball falls, since the upward force is no longer sufficient to support it. That there is still a horizontal force acting on the ball when the displacement is much greater than 1.0 cm. can be shown, however, by suspending the ball with the cotton vertical and gradually bringing the air-jet nearer to the ball, the vertical distance between them being 13.5 cm. as before. When the axis of the jet is about 5.0 cm. from the centre of the ball the latter is drawn into the stream of air and lies approximately on the axis of the jet with the cotton inclined at an angle to the vertical.

AN X-RAY STUDY OF THE SUPERLATTICE IN CERTAIN ALLOYS

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ABSTRACT. Superstructures in the β phases of silver-zinc and gold-zinc alloys submitted to various heat treatments have been investigated. Whereas in the gold-zinc alloys the atoms were found in ordered arrangement both in quenched specimens and in specimens maintained at temperatures up to the melting points of the alloys, in the silver-zinc alloys ordered arrangement of atoms in the lattice was found only in quenched alloys. The results obtained are discussed in the light of the theory of order and disorder in alloys, put forward by Bragg and Williams.

§ 1. INTRODUCTION

THE conditions under which superlattices are formed has been the subject of much theoretical and experimental research in recent years. Tammann⁽¹⁾ found that long annealing of an alloy produced a change in its resistance, and to explain this he suggested that the heat treatment had caused a change from a disorderly to an orderly distribution of atoms in the crystal lattice. Johansson and Linde⁽²⁾, examining the gold-copper alloy system by an X-ray method, found that such a rearrangement of atoms did occur. Observations carried out by Haughton and Payne⁽³⁾ and by Kurnakow and Ageew⁽⁴⁾ on the change in electrical resistance corroborated these results. Another notable contribution in this field is that of Bradley and Jay⁽⁵⁾, who made a comprehensive X-ray study of the problem as presented in the iron-aluminium alloy system.

The theoretical side of the problem has been studied by many workers, including Gorsky⁽⁶⁾, Borelius, Johansson and Linde⁽⁷⁾, Dehlinger and Graf⁽⁸⁾, Bragg and Williams⁽⁹⁾ and Bethe⁽¹⁰⁾. The general conceptions are similar in all treatments.

Bragg and Williams assume that at very low temperatures the equilibrium state of an alloy is one of perfect order. As the temperature rises the equilibrium degree of order decreases, slowly at first then more quickly, until complete disorder is reached at a certain critical temperature T_c , this temperature being characteristic of the alloy. Above T_c the alloy has a completely random distribution of atoms. By considering the time of relaxation of an alloy, that is the time of annealing required at any particular temperature to bring the alloy into equilibrium, these

authors are able to define two temperatures, T_q and T_a , such that alloys quenched from above T_q will always have the atomic distribution characteristic of the equilibrium condition at T_q , while any practicable time of annealing below T_a will fail to change the condition of the alloy. By quenching from any temperature between T_a and T_q the equilibrium condition at that temperature will be retained. According to the relative values of T_a , T_q , T_c and T_m (the melting point of the alloy), the following four possibilities arise.

Case 1. $T_c < T_a < T_q < T_m$. Although at low temperatures the equilibrium state has a certain degree of order, it will be impossible to obtain an alloy in this state since when cooling from the melt, the temperature T_a is reached while there is still complete disorder.

Case 2. $T_a < T_c < T_q < T_m$. Alloys with any degree of order equal to or less than that characteristic of T_a can be obtained by quenching from the appropriate temperature.

Case 3. $T_a < T_q < T_c < T_m$. In this case, although the equilibrium condition of the alloy between the temperature T_c and T_m is one of disorder, it will be impossible to retain this condition on quenching. All the alloys, whatever their thermal history, will have a certain degree of order at low temperatures.

Case 4. $T_a < T_q < T_m < T_c$. The equilibrium condition of alloys at all temperatures has a certain degree of order.

The experiments of Sykes⁽¹¹⁾ on the variation of specific heat in CuZn and FeAl alloys furnish evidence in support of the above theory.

In the course of a detailed study of the silver-zinc system of alloys, an account of which will appear elsewhere, superlattice lines were observed on certain spectrum photographs of the β alloys. It was resolved to examine these alloys more fully, both at low and at high temperatures, and to investigate similarly the analogous phase in the gold-zinc system. The possible existence of the temperature T_q , as suggested by Bragg and Williams, from above which it is impossible to retain the state of the alloy on quenching, could thus be investigated. Only alloys containing approximately 1 : 1 atomic ratio of constituents will be dealt with here. To obtain quantitative results, measurements of the intensities of the reflection lines are necessary, but these have not been made on the spectra which will be considered in this paper.

§ 2. THE β PHASE OF SILVER-ZINC

The β phase in the silver-zinc system extends at 300° C. from 49.4 to 54.3 atomic per cent of silver and widens as the temperature increases; at 600° C. it extends from 49.2 to 58.2 atomic per cent of silver. It possesses a body-centred cubic structure which changes to a close-packed hexagonal one below the transformation temperature which varies between 289° C. and 264° C. according to the composition of the alloy. The transformation differs from that of the β phase of copper-zinc where the body-centred cubic structure is retained below the transformation temperature.

Westgren and Phragmen^(1a) obtained superlattice lines in spectrum photographs of a silver-zinc alloy containing 49.5 atomic per cent of silver taken at room temperature, but they did not pursue the matter further.

In the present investigation, the first spectrum photograph taken of an alloy which had been quenched from the pure β region was that of alloy 51.2,* annealed at 410° C. for 12 hr. The strongest lines in the spectrum were due to reflections from the planes, for which $Q^2 (\equiv h^2 + k^2 + l^2) = 2, 4, 6, 8, 10, 12$, of a cubic lattice, the parameter of which was about 3.150 Å. These are the lines to be expected from a body-centred cubic structure. In addition to these lines, there were present fainter reflections from planes of the same cubic lattice for which $Q^2 = 3, 5, 9, 11$. These last reflections showed that the centre and corners of the unit body-centred cubic cell were not structurally equivalent; there was a certain amount of segregation of the silver atoms to the corners and zinc atoms to the centres of the cubes (or vice versa). Another specimen from the pure β phase, alloy 53.0, annealed at 535° C. for 9 hr. and quenched, also gave superlattice lines.

Alloys quenched from the $(\alpha + \beta)$ region also yielded spectra with superlattice lines, but the lines were fainter than those obtained with the pure phase alloys. The following are particulars of the heat treatments given to the alloys from the $(\alpha + \beta)$ region which were investigated: (1) Alloy 55.2, annealed at 331° C. for 29 hr. and quenched. (2) Alloy 59.2, annealed at 535° C. for 9 hr. and quenched. (3) Alloy 58.0, annealed at 448° C. for 72 hr. and quenched.

The results of the measurements made on the photograph taken with alloy 59.2 using cobalt K_α radiation with an iron filter, are included in table 1. The superlattice lines in the β phase were very faint but measurable and they yielded consistent values of the lattice parameter.

Table 1

Strength of reflection	Corrected arc (mm.)	log sin	Radiation	Reflection planes	α phase parameter (Å.)	Reflection planes	β phase parameter (Å.)
<i>s</i>	210.57	1.5879	K_α	(111)	3.998	—	—
<i>f</i> +	208.03	1.6019	K_α	—	—	(110)	3.161
[<i>vf</i>]	198.76	1.6498	K_α	(200)	4.003	—	—
<i>c</i> 189	—	—	K_α	—	—	(111)	c. 3.15]
<i>m</i>	173.90	1.7522	K_α	—	—	(200)	3.162
<i>m</i>	158.98	1.8002	K_α	(220)	4.004	—	—
<i>s</i>	144.38	1.8403	K_α	—	—	(211)	3.162
<i>m</i> +	132.04	1.8691	K_α	(311)	4.007	—	—
<i>m</i>	123.03	1.8881	K_α	(222)	4.006	—	—
	115.45	1.9027	K_α	—	—	(220)	3.162
[<i>vf</i>]	100.0	1.9281	K_α	—	—	(300)	3.164]
<i>s</i>	83.58	1.9506	K_α	(400)	4.006	(310)	3.167
[<i>vf</i>]	64.2	1.9712	K_α	—	—	(311)	3.167]
<i>s</i>	43.21	1.9871	K_{α_1}	(331)	4.009	—	—
<i>s</i>	41.60	1.9880	K_{α_1}	(331)	4.008	—	—
<i>s</i>	38.41	1.9898	K_{α_1}	—	—	(222)	3.166
<i>s</i>	36.58	1.9908	K_{α_1}	—	—	(222)	3.165

* Alloy 51.2 means an alloy containing 51.2 atomic per cent of silver. This method of referring to the alloys will be adopted throughout the paper.

Difficulty was encountered in retaining the high temperature structures of alloys in the $(\beta+\gamma)$ region. Since the β component breaks down readily into the ζ phase, and the γ component gives a large number of spectral lines, it was impossible to tell with certainty whether the superlattice lines were present in photographs of quenched alloys in the $(\beta+\gamma)$ region.

The next step was to study the effect of quenching pure β -phase alloys from still higher temperatures. Three samples of alloy 53.0 were subjected respectively to the following heat treatments: (1) annealed at 650° C. for 30 min. and quenched, (2) annealed at 672° C. for 8 min. and quenched, (3) annealed at 691° C. for 7 min. and quenched. According to the equilibrium diagram published in the *International Critical Tables*, the alloy when annealed at 691° C. should be in the $(\beta + \text{liquid})$ region. The spectra obtained with the three specimens gave superlattice lines which appeared as strong as the lines obtained with specimens annealed at lower temperatures. The superlattice exists therefore up to the highest temperature at which the alloy's structure can be retained by quenching.

Evidence of the existence of a superstructure in all quenched alloys having been obtained, it remained to examine the alloys at high temperatures.

Alloy 53.0 was again used. It was annealed at 500° C. for 2 hr. in vacuo* and then a photograph was taken at 500° C., which occupied another period of 2 hr. No superlattice lines were observed but the lines from the body-centred cubic structure were also rather weak in the photograph so that the result was not conclusive. A similar result was obtained with another specimen of the alloy which had been annealed at 450° C. for 21 hr. A better photograph was obtained with the same alloy after a shorter period of annealing. When the specimen was kept at 400° C. for 15 min., before being exposed at this temperature for 1 hr. 45 min., the resulting spectrum contained strong well-defined lines from the body-centred cubic lattice but superlattice lines were absent. This experiment showed that the β phase was quickly formed at these temperatures.

It was feared that volatilization of the zinc might vitiate the results, although it had previously been ascertained that volatilization was slight in these alloys at temperatures below about 400° C. In order to reduce the effect as much as possible, the temperature of annealing was reduced to that just above the transformation temperature of β to ζ phase which at its maximum is about 289° C. Alloy 50.25 was accordingly annealed at 303° C. for 4 hr. 30 min. and then exposed at 303° C. for 1 hr. 30 min. Although in this photograph the contrast between the background and the spectral lines from the body-centred cubic planes was as good as that in the most successful photographs obtained with quenched alloys, there was no trace of superlattice lines.

It was considered possible that the equilibrium state of the alloys at this comparatively low temperature was one of order, but that the kinetic energy of the atoms might not be sufficient to cause much interchange of atoms. In this case if the β lattice, when first formed from the hexagonal lattice, had a random distri-

* All the specimens examined at high temperatures were maintained at these temperatures and exposed to the X-ray beam in vacuo.

bution of atoms, this distribution would remain random until the alloy was heated to a temperature considerably above 300°C . This possibility was disproved however by the following experiment. An alloy was heated below the transformation temperature for 2 to 3 hr. to ensure that the β lattice was destroyed. It was then annealed for 4 hr. between 295 and 303°C . and quenched, the latter temperature never being exceeded. The alloy when photographed gave good superlattice lines. The spectra are reproduced in figure 1. Hence an alloy in the pure β phase of silver-zinc quenched from a temperature of about 300°C ., which is about 20°C . above the transformation temperature for the particular alloy examined, yielded strong superlattice lines, but the same alloy maintained at 300°C . yielded a spectrum in which there was no indication of a superstructure.

It was of interest to examine an alloy in the $(\alpha + \beta)$ region at elevated temperature. Accordingly alloy 55.1 which at 300°C . is in the $(\alpha + \beta)$ region, and situated nearer to the $(\alpha + \beta) - \beta$ than to the $\alpha - (\alpha + \beta)$ boundary, was studied.

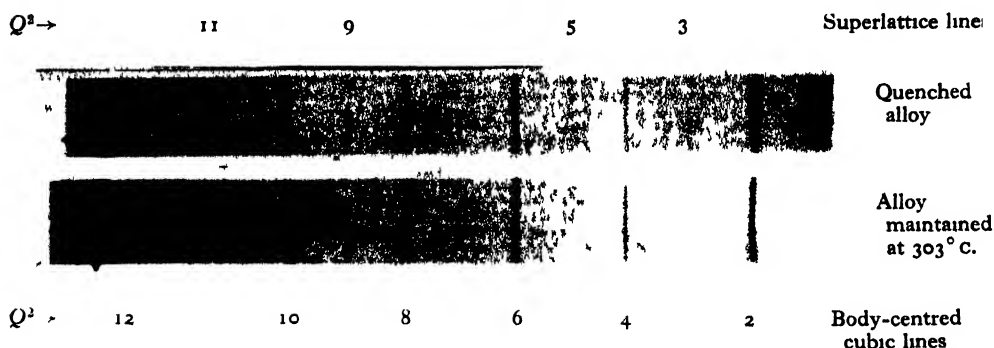


Figure 1. Superlattice lines in a quenched silver-zinc β phase alloy, but none at 303°C

The alloy was mounted on the camera and maintained in vacuo at 300°C . for 3 hr. prior to the X-ray exposure at this temperature, which occupied a further period of 2 hr. The alloy was not a good reflector at high temperature and did not yield satisfactory lines. It was found necessary to increase the X-ray exposure to 4 hr. but even then the lines were not as intense as could be desired. Several photographs were taken but in each case the lines were very faint, and it was impossible from these photographs to state with certainty that the superlattice lines were absent. Improved conditions of exposure yielded better spectra, but no superlattice lines could be observed in the β -phase spectrum.

The lattice-dimensions of the component phases in a mixed region can be retained up to the melting point of the alloy, but the atoms may not be orderly distributed throughout the lattice at these temperatures. Order amongst the atoms in the lattice seems to set in at a comparatively low temperature. It would appear that a change in the size of the lattice entails a far greater disturbance of the atoms than does a change from disorder to order.

It is concluded from these experiments on silver-zinc alloys that

- (i) All quenched pure β -phase alloys show superlattice lines. Therefore $T_q < T_c$,

(case 3 or case 4); that is, a certain degree of order exists at all temperatures below T_q , the highest temperature at which the structure can be retained by quenching.

(ii) No pure β -phase alloys gave superlattice lines at high temperatures including 500, 450, 400 and 303° C. Hence $T_c < 303^\circ \text{C.}$ and by (i) $T_q < T_c < 303^\circ \text{C.}$, that is the highest temperature at which the property of ordered arrangement in the pure phase β lattice can be retained by quenching is less than some temperature T_q which is itself less than 303° C. The transformation temperature of β to ζ varies between 264 and 290° C. for alloys of different compositions.

(iii) Alloys in the $(\alpha + \beta)$ region, in which the β phase is saturated, when quenched from 331, 448 and 535° C. showed superlattice lines. Hence $T_q < T_c$ as in (i) above.

(iv) Alloys in the $(\alpha + \beta)$ region showed no β -phase superlattice lines at high temperatures. In this case T_q is less than the lowest temperature at which the alloy can be examined above the transformation temperature. But the size of the lattice can be retained by careful quenching from temperatures up to 600° C., and without much difficulty up to 450° C. There is therefore a different temperature T_q for the two properties, (a) the size of the lattice, and (b) the ordered distribution of the atoms.

If the atomic distribution were entirely random at high temperatures, it would be expected that the beginning of the ordering process would be slow, as initially there would be no right and wrong positions, as they may be called, for the atoms, but this does not appear to be the case. To explain the results obtained with quenched and heated specimens of silver-zinc alloys, it could be assumed either (1) that the silver and zinc atoms are able at high temperatures to interchange positions rapidly resulting in a random distribution and that this random interchange persists until a comparatively low temperature is reached, when order sets in, or (2) that the structure at high temperature is not entirely random but possesses a certain degree of order of a type which is not revealed by X-ray examination. For instance, the silver and zinc atoms may be paired off, that is, the movement of a certain silver atom may be closely associated with that of a certain zinc atom. This would require, as in J. J. Thomson's dipole theory, entities similar to dipoles (polarized molecules), the axes of which are oriented at random at the higher temperatures within the limitations set by the crystal structure but tend to the same orientation at some lower temperature when the disturbance due to the thermal vibration becomes small compared with that due to the forces of the crystal lattice.

Although the structure does not possess a superlattice at high temperatures, the readjustment of the atoms required to produce such a superlattice may be small compared with that required to change the size of the lattice or to change the structure of the crystal. On quenching, the cooling is rapid enough to prevent the pure β -phase alloys from changing into the hexagonal ζ structure, but at some temperature in the cooling process the silver and zinc atoms settle into positions of least potential energy in a body-centred cubic lattice. The critical temperature T_c at which this rearrangement of the atoms begins may be anything below that of quenching, and it may be well below the temperature at which transformation

to the ζ phase normally takes place. The temperature T_c is certainly below 303°C. in the pure β phase as is shown under (ii) above.

Weerts⁽¹³⁾ also found that superlattice lines obtained with quenched alloys were absent when the alloys were examined at high temperatures. He sought to explain this by suggesting that the atoms in the β phase were distributed at random in the lattice but that they became ordered on quenching.

§ 3. THE β PHASE OF GOLD-ZINC

The β phase of gold-zinc, like that of silver-zinc, possesses a body-centred cubic structure. According to the accepted equilibrium diagram of this system, the β phase of gold-zinc differs from the β phase of silver-zinc in that the former does not transform to another phase at low temperature. Westgren and Phragmen⁽¹²⁾ obtained superlattice lines with a gold-zinc β -phase alloy at room temperature.

For the present investigation a gold-zinc alloy was prepared by melting a mixture of gold and zinc filings in an evacuated silica tube, the mixture being well shaken while it was molten. Specimens of the alloy in powder form were given the following heat treatments before being photographed at room temperature. Alloy 50.8 containing 50.8 atomic per cent of gold: (1) annealed at 250°C. for 76 hr. and quenched; (2) annealed at 603°C. for 6 hr. and quenched; (3) annealed at 720°C. for 18 min. and quenched.

All three spectra contained strong superlattice lines showing that this β -phase alloy consisted of two interpenetrating simple cubic lattices, one of gold and the other of zinc atoms, the corner of a unit cell of the one being at the centre of a unit cell of the other. The spectrum obtained after heat treatment (3) above is shown at the top of figure 2. The equilibrium diagram of the gold-zinc system gives 726°C. as the melting point of a β -phase alloy. The superstructure is thus present in alloys quenched from all temperatures up to within a few degrees of the melting point.

Five high-temperature photographs of the alloy were taken; the results are shown in the table:

Temperature ($^\circ \text{C.}$)	Remarks
400	Superlattice lines present.
528	Superlattice lines present but also a trace of α -phase lines showing volatilization of zinc.
560	Distinct superlattice lines but a fair amount of α phase present
577	Faint superlattice lines, which appear to be fainter in relation to the body-centred cubic lines than are those in photographs taken at lower temperatures. The α -phase lines had increased in intensity.
640	No trace of β -phase lines. The only lines present were from a face centred cubic lattice and the doublets were well resolved. All the zinc had volatilized before the exposure was started, leaving gold.

The photographs are reproduced in figure 2. The spectra show that the superlattice exists up to a temperature of 577°C. at least, though the photograph taken

at this temperature suggests that it may disappear at still higher temperatures. If this be so, the photographs obtained with quenched alloys indicate that the equilibrium state at these high temperatures cannot be retained by quenching. But there may be some cause additional to the heat motion of the atoms to account for the faintness of the superlattice lines at the higher temperatures.

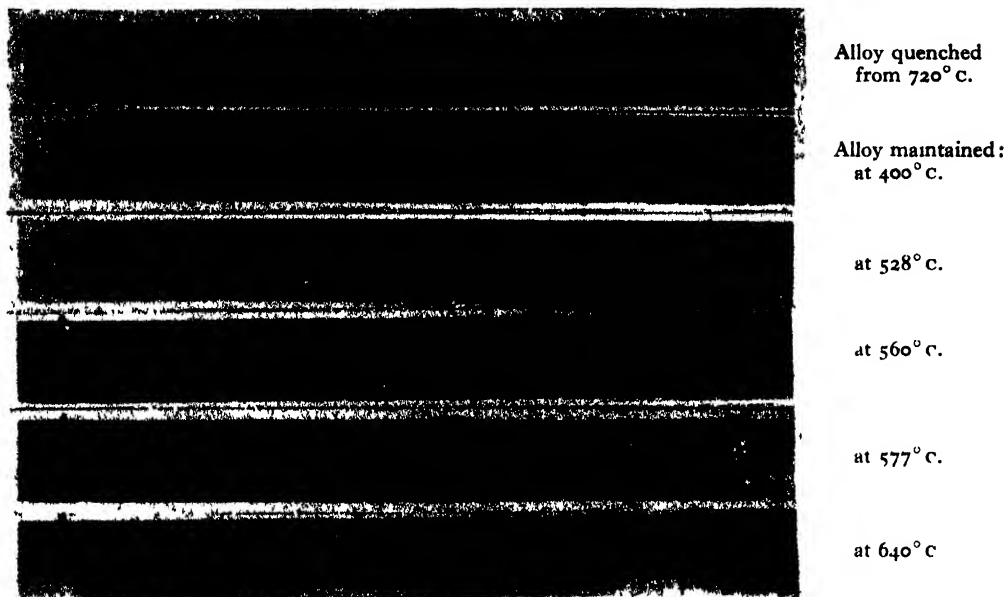


Figure 2. Superlattice lines in a quenched gold-zinc β -phase alloy and in the same alloy when maintained at high temperatures

After this work had been completed a reference to an investigation by Soldau⁽¹⁴⁾ was found. In his paper it is recorded that superlattice lines were obtained with β -phase gold-zinc alloys at temperatures up to 550° C.

The results of the work on β -phase gold-zinc alloys may be summarized in the following statement. In alloys quenched from temperatures up to the melting point a superstructure is present. This superstructure is also present at temperatures ranging from 400 to 577° C. and possibly at higher temperatures up to the melting points of the alloys.

§ 4. CONCLUSIONS

The behaviour of a 50-atomic-per-cent alloy of silver-zinc under various heat treatments differs from that of a 50-atomic-per-cent alloy of gold-zinc subjected to similar heat treatment. Whereas with the latter the atoms are orderly arranged both in quenched specimens and specimens maintained at temperatures in the range extending from room temperature to the neighbourhood of the melting point of the alloy, in the former an orderly arrangement of atoms in the lattice was

found only in quenched alloys. A random distribution of atoms in the lattice was found in alloys maintained at temperatures between 300° C. and the melting points of the silver-zinc alloys. Below about 300° C. a transformation of the body-centred-cubic β phase to the hexagonal ζ phase takes place. No such change of structure has been observed in this region for gold-zinc alloys. This difference between the phase fields in this region of composition in the two alloy systems may account to some measure for the difference in behaviour between the alloys.

Both alloys may be considered under cases (3) and (4) of Bragg and Williams mentioned above. In the gold-zinc alloys the critical temperature T_c may be higher than the melting point T_m , and T_q may be as high as the melting point. This alloy would therefore come under case (4). But the present investigation does not enable a definite distinction to be made between cases (3) and (4), for volatilization of zinc made it impossible to ascertain the highest temperature at which the superstructure existed. Quenched alloys, although they showed the presence of superstructure up to the highest temperature of quenching, which was close to the melting point of the alloy in each case, did not supply the information required as to the relative values of T_q and T_c .

With the silver-zinc alloys which were maintained at elevated temperatures it was possible to show quite definitely that for these alloys $T_q < T_c < 300^\circ \text{C}$. That is, a pure β -phase alloy had a critical temperature close to the transformation temperature, and T_q may be at or below the transformation temperature.

It is suggested that there may be in alloys at high temperature some type of order which cannot be detected by X-rays. This suggestion is based on the behaviour of the β phase in simple and duplex regions.

The present investigation is to be regarded as preliminary to a more detailed examination of these and other alloys which is now in progress.

§ 5. ACKNOWLEDGEMENT

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THE RELATIVE LUMINOSITY OF RADIATION AT WAVE-LENGTHS 5780 AND 5461 Å. FOR THE AVERAGE PHOTOMETRIC OBSERVER

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ABSTRACT. The relative luminosity of radiation of wave-lengths 5780 and 5461 Å. has been determined for sixteen observers whose mean Y/B ratio was 1.003, using the Guild flicker photometer with 2° field, and a field illumination of 25 to 30 lux. The corresponding relative energy measurements were made with a calibrated emission type photocell. The source of light was a high-pressure mercury discharge lamp with selective colour filters to isolate the two spectrum lines concerned. The results show good agreement with the value based on the luminosity factors adopted internationally in 1924 by the Commission Internationale de l'Éclairage. The paper includes details of the filters used, the method of calibration of the photocell, and investigations on the linearity of response and possible colour-selectivity of the thermopile used for the calibration. The question of the influence of field-size on the results is examined and discussed also.

§ 1. INTRODUCTION

IN 1924 the Commission Internationale de l'Éclairage officially adopted a table⁽¹⁾ of values of the relative visibility or luminosity factor based on the average values for a large number of colour-normal observers, previously determined by a number of investigators, notably Gibson and Tyndall. The conditions and results of these determinations are summarized by Gibson⁽²⁾. These C.I.E. standard luminosity factors form the fundamental basis of the colour test using the yellow/blue (or Y/B) ratio for the classification of the colour properties of photometric observers⁽³⁾, and also the basis of all methods of heterochromatic photometry using minimum colour-difference and a small field, such as the flicker method and the use of colour-match filters for direct comparison. More recently, however, Arndt⁽⁴⁾ and Dresler⁽⁵⁾, and Federov and Federova⁽⁶⁾ have re-examined the validity of the standard luminosity curve.

Federov and Federova used the cascade method with 1.5° field, full light-adaptation and daylight illumination in the photometer room. Their determinations were made throughout the spectrum, but the values deduced from their results for the relative luminosities at 5780 and 5461 Å. are given as 1.028 and 1.095 for the two investigators respectively.

Arndt and Dresler both used the powerful sources of monochromatic light now available in the form of electric discharge lamps. They used a Bechstein flicker

photometer for visual comparison of different spectrum lines, and a calibrated selenium rectifier photocell as intermediary for the necessary relative energy determinations. The field size of the flicker photometer was 1.5° or less, and a bright surround field was used to obtain light adaptation. Arndt determined the relative luminosity for the yellow and green mercury lines, obtaining a value $K_{5780} : K_{5461} = 1.035$ for the average of some 50 observers, while Dresler extended the wave-length range to include the sodium yellow doublet, obtaining $K_{5893} : K_{5461} = 0.94$ for the average of 34 observers. These values were obtained for a field illumination of about 30 lux.

None of these four investigators gives information as to the Y/B ratios of the observers concerned in the measurements, but all are agreed in stressing the importance of reducing the field-size to about 1° in order to ensure pure cone-vision. They infer that this reduction is mainly responsible for the difference between their results and the figures derived from the C.I.E. standard values, which are $K_{5780} : K_{5461} = 0.899$ and $K_{5893} : K_{5461} = 0.781$, the third significant figure here depending, within a range of 3 or 4, on the method of interpolation used.

By examining the data summarized by Gibson⁽²⁾, one can also obtain the values shown in table 1 on the basis of the determinations of relative luminosity made by the investigators whose work was considered in the derivation of the C.I.E. standard table. With some exceptions the field illumination used by these investigators was of the order of 25 lux. The pupil conditions at the eye itself were not exactly specified.

Table 1

Investigators	Field-size	$K_{5780} : K_{5461}$
Hyde, Forsythe and Cady	8°	0.887
Gibson and Tyndall	3°	0.894
Ives-Nutting	2°	0.910
Coblentz and Emerson	2°	0.931

Here the differences among the figures in the last column are considerably smaller than that between the figures obtained by Arndt, and Federov and Federova, and that based on the C.I.E. standard luminosity factors. This is so despite the fact that rod vision would be operative to an appreciable extent in the 8° field used by Hyde, Forsythe and Cady, and the 3° field of Gibson and Tyndall, but relatively inappreciable for the 2° field employed in the other two cases included in table 1.

In view, therefore, of the departures of the more recently determined values from the C.I.E. standard luminosity factors, it is of importance to examine again the validity of the latter under the experimental conditions to which they most nearly apply. Although not specifically laid down, these may be stated as follows: Field-size, 2° with minimum colour-difference; apparent field-brightness, 25 to 30 equivalent lux; surround field of similar brightness, and of size 20 to 30° ; normal unrestricted pupil diameter; darkened photometer room.

It should be noticed here that the value to the photometrist of the C.I.E. standard factors lies in their reproducibility under set conditions, suitable for general photometric purposes, rather than in any specific visual characteristic which they may represent. They are intended to define, under the specified conditions, a photometric scale adequately representative of possible observers.

The present paper describes a series of measurements on the ratio $K_{5780} : K_{5461}$ on the same general lines as Arndt's investigation, but using a Guild flicker photometer⁽⁶⁾ for the visual work, and a calibrated vacuum emission photocell for the measurements of relative energy. It also describes the tests made to ensure the accuracy of the calibration of the cell, and to arrive at as complete a knowledge of its characteristics as possible. Sixteen colour-normal observers took part, and their Y/B ratios are given in the table of results. A further examination was also made of the influence of a reduction in field-size from 2 to 1°, twelve observers taking part.

§ 2. PRINCIPLES OF THE METHOD

A Guild flicker photometer *G*, figure 1, and a photoelectric photometer *P*, using the calibrated photocell, were mounted one above the other, as close together as possible, in a fixed position on a photometer bench. Beyond the end of the bench

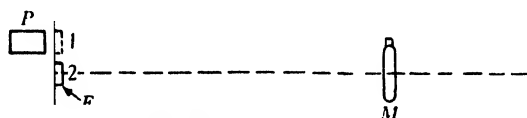


Figure 1. Photometric system.

a 250-w. mercury discharge lamp *M* was mounted at a fixed distance from the photometers. Light from *M* was incident on the photocell in *P* and also on the rotating vanes of *G*. A tungsten lamp *L* of the uniplanar-filament type was movable on the bench to provide the comparison source for measurements made with *G*, and illuminated the fixed test surface of *G* via the usual mirror contained in *G*. Any selectivity in this mirror therefore affected only the constant comparison source, and introduced no error in the comparative measurements of the radiation from *M*. The test surfaces of *G* were freshly smoked with an adequate thickness of magnesium oxide, whose colour-selectivity is known to be negligible^(8,9).

The flicker photometer had a large exit pupil, a 2° field, and a surrounding field set to a brightness slightly lower than that of the flicker spot. The desired spectrum line of *M* was isolated by a filter located at *F* and movable in a slide *S* so as to cover *P* or *G* at will.

The sequence of measurements was as follows: (1) Filter for green line in position 1; reading on *P*. (2) Filter for green line in position 2; ten visual observations by each of two observers on *G*, with movable comparison lamp. (3) Filter for green line in position 1; check reading on *P*. (4) Filter for yellow line in

position 1; reading on *P*. (5) Filter for yellow line in position 2; visual observations on *G*. (6) Filter for yellow line in position 1; check reading on *P*. We then have

$$\frac{K_{5780}}{K_{5461}} = \frac{(5)}{(2)} \times \frac{\text{mean of (1) and (3)}}{\text{mean of (4) and (6)}} \times \frac{S_{5780}}{S_{5461}},$$

where S_{5780}/S_{5461} is the ratio of the sensitivities of the photocell per unit incident energy of the wave-lengths concerned.

The above sequence of measurements was repeated for other pairs of observers, and for the same pairs on different occasions. Its shortness, in time, avoided the effect of possible changes in transmission of the filters due to changes in temperature, and also provided frequent checks on the constancy of *M* by means of the high-precision photoelectric readings. *M* was operated on alternating current, the value of this current being kept constant, and the distances of *M* and *L* from the photometers were arranged to give an illumination at the photometer within the range 25 to 35 lux.

One point assumed in the above method is that the composition of the radiation from *M* falling on *P* is identical with that incident on *G*. There seems no reason to doubt the validity of this assumption in view of the relatively large distance between *M* and *G* (over 1½ m.).

§ 3. CALIBRATION OF THE PHOTOCCELL

The photocell used was a vacuum cell of the Osram KMV 6 type operated at a voltage giving approximate saturation. In order to avoid trouble due to uncertainty of light-distribution on the cathode it was calibrated and used throughout in conjunction with a disc of Ilford diffusing medium mounted at a short fixed distance in front of the cell. All the figures given for relative colour-sensitivity of the cell therefore include any selectivity in this diffuser.

The first spectral calibration was carried out in November 1936, on the spectrophotometer apparatus described by Preston and Cuckow⁽¹⁰⁾, with a tungsten-filament lamp as light-source, and a linear thermopile in the telescope slit to determine the relative transmitted energy at various wave-lengths. The wave-length calibration of the spectrometer was carefully checked beforehand by means of the iron and copper arcs. Precautions were also taken to ascertain whether the small fraction of radiation escaping between the targets of the thermopile (and therefore the percentage falling on the thermopile) was reasonably constant throughout the spectrum. Photoelectric measurements showed that this was so. Further precautions were taken to eliminate the effect of stray light in the spectrometer by the use of appropriate colour filters to assist in purifying the light. A result

$$S_{5780} : S_{5461} = 0.688$$

was obtained.

By a similar method, but with a 125-w. extra-high-pressure mercury tube as source of light in conjunction with the spectrometer and the actual photoelectric photometer used subsequently, a value of 0.709 was obtained in the same month.

Both methods were repeated after the present work (August 1937) and values 0.698 and 0.715 respectively were obtained. The photocell thus appeared to be sufficiently stable, and a final mean value of $S_{5780} : S_{5461} = 0.702$ was adopted, the probable error on this figure being $\pm 1\frac{1}{2}$ per cent.

§ 4. {ILLUMINATION, CURRENT} CHARACTERISTIC OF THE PHOTOCELL

The {illumination, current} characteristic of the cell was checked by the methods described by Preston and McDermott⁽¹¹⁾ and Preston and Cuckow⁽¹⁰⁾ and was found to be linear within a few parts in 10,000 over the range of photocurrents and wave-lengths applicable to the present investigation.

§ 5. CHARACTERISTICS OF THE THERMOPILE

The use of the thermopile for measurements of relative energy involves two assumptions: first, that the thermal e.m.f. developed is proportional to the absorbed energy (of constant wave-length) over the range of measurement; and secondly, that the absorbed energy is a constant percentage of the incident energy over the range of wave-lengths concerned, i.e. the thermopile is non-selective.

The first assumption was examined by comparison of the readings of the thermopile with those of the photocell itself, when the two were exposed in turn to varying amounts of radiation of constant wave-length. The characteristic of the thermopile was not found to deviate from that of the photocell by more than a few parts in 10,000 and may therefore be regarded as linear to an accuracy well within that required.

The second assumption was examined in two ways. In the first, the thermopile targets were strongly illuminated by a steady mercury lamp and an image of them was focused on the collimator slit of the photoelectric spectrophotometer. The ratio of the readings given by the yellow and green mercury lines was noted, the telescope slit being wide enough to accept the entire image in each case. The thermopile was then replaced by a fresh surface of magnesium oxide and the ratio was again noted. The difference between these ratios indicates the difference between the reflection factors of the targets for the light of the two mercury lines, assuming the magnesium oxide to be non-selective. With care to avoid conditions of specular reflection a difference of about 5 per cent was recorded. Since, however, the absolute reflection factor of the targets was found by the same experiment to be approximately 4 per cent, this difference in reflection factor corresponds to a difference in absorption factor of only about 0.2 per cent as between the two wave-lengths considered. This is negligible for the present purpose.

In the second method a direct calibration of the photocell was attempted, the spectrometer set-up being used. The collimator slit was directly illuminated by a tungsten-filament lamp of known colour temperature and the ratio of the readings was noted when the wave-length was set successively to 5780 and 5461 Å., constant slit-widths being used. Given the distribution of relative energy of the source, the

dispersion correction of the spectrometer, and its relative optical transmission* at the two wave-lengths, the relative transmitted energy could be calculated and the relative sensitivity of the photocell obtained. Unfortunately the optical transmission of the spectrometer was not known, but it was assumed to be the same for the two spectrum lines, in view of their narrow separation. With this assumption, the value of $S_{5780} : S_{5461}$ obtained differed from the mean of the other determinations by only 1 part in 700, and the method may therefore be regarded as confirming the correctness of this mean value.

§ 6. THE COLOUR FILTERS

The filters used to isolate the lines were: (1) For 5780 Å., a Chance-Parsons deep orange glass No. 3 of thickness 3.68 mm. together with 1 cm. of a 0.3-M. aqueous solution* of cupric chloride. (2) For 5461 Å., a Chance didymium glass, of thickness 10.00 mm., with Chance-Parsons green glass no. 5, of thickness 2.78 mm. All the components, including the liquid-cell, were optically worked. The spectral transmission curves are shown in figure 2, while the transmission value for the principal mercury lines are shown in table 2.

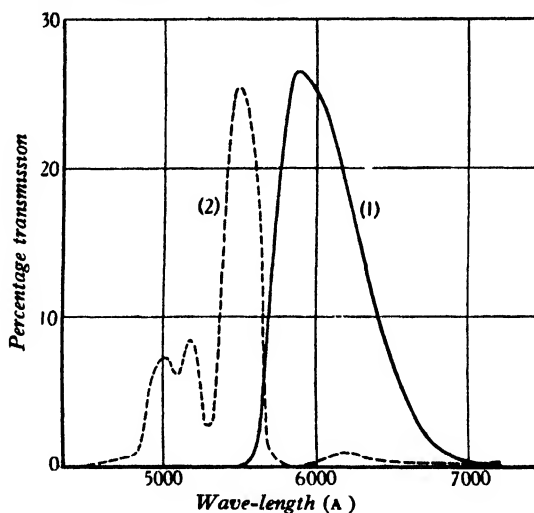


Figure 2 Spectral transmission of filters (1) and (2).

Table 2

λ (Å.)	T (per cent)	
	(1)	(2)
5780	21.74	0.04
5461	0	17.9
4916	0	4.8
4358	0	0
4046	0	0

* M stands for the molecular weight in grams per litre of solution.

The combination (1) transmits a certain amount of the continuous background at the red end of the spectrum of the mercury discharge lamp, but calculation shows that this amount is unimportant in the case of the 250-w. lamp used. The calculated purity of the radiation transmitted by the filters, based on relative energy values given by Taylor and Kerr⁽¹²⁾, is in both cases well over 99 per cent.

It is to be noted that both filter combinations have sharp cut-offs of the type showing temperature effects. This necessitated short cycles of measurements, as described in § 2.

§ 7. USE OF ALTERNATING CURRENT FOR THE LIGHT-SOURCE

The discharge lamp *M* was operated throughout the main investigation on alternating current, for which it was designed. The object was to preserve the steadiness and constancy of the lamp as well as possible for the considerable time during which it was alight. On the other hand, stroboscopic effects due to this fact were not entirely absent from the field of the flicker photometer. It was therefore thought desirable to ascertain whether the photometric balance was affected thereby in any systematic way. Results of previous tests in the Photometry Division of the National Physical Laboratory were available, and revealed no systematic difference. In the present case, however, a further experimental test was made by four observers under conditions identical with those of the main investigation, and this again revealed no systematic difference between results obtained with *M* operated on alternating and direct-current supplies respectively. The actual mean observed difference was $\frac{1}{2}$ per cent, which is well within the limits of experimental error.

§ 8. EFFECT OF FIELD-SIZE IN THE FLICKER PHOTOMETER

In view of the importance assigned by various authors to the matter of field-size it was considered desirable to investigate whether a reduction from the normal 2° field of the Guild flicker photometer to 1° would influence the results by a more complete elimination of rod vision. A removable stop was therefore made to fit over the 2° aperture of the photometer, to reduce the field-size to 1° , forming at the same time a continuation of the illuminated surrounding field provided in the instrument. In order to obtain the highest precision in the comparison of results obtained for the two field-sizes respectively the lamp *M* was operated on direct current. A photometric comparison of the two filtered radiations from *M* was then carried out using the flicker photometer, each observer using the 1 and 2° fields successively. Observers worked in pairs to avoid fatigue. No attempt was made to obtain any absolute values of $K_{5780} : K_{5461}$ from this subsidiary investigation, so that photoelectric readings were omitted. In other respects, however, the conditions were identical with those under which the results in § 9 were obtained.

The results are in table 3, the figure given being the ratio of the two figures proportional to $K_{5780} : K_{5461}$ obtained by each observer using field-sizes of 1 and 2° respectively.

Table 3

Observer	$\frac{[K_{5780} : K_{5461}]_{1^\circ}}{[K_{5780} : K_{5461}]_{2^\circ}}$	Observer	$\frac{[K_{5780} : K_{5461}]_{1^\circ}}{[K_{5780} : K_{5461}]_{2^\circ}}$
HFM	0.990	FJCB	1.021
GEVL	0.963	JSP	0.944
GCC	0.999	BJO	0.982
HRS	0.979	GWGS	0.973
LHMcD	0.997	WB	0.991
FMH	0.975	HB	0.964
Mean ratio = 0.980			

It is seen from the table that all the observers except one obtain a lower figure for the yellow/green luminosity ratio when using the smaller field. As a whole the results appear to show definitely a systematic field-size effect. The amount of the effect is, however, small, the mean change in relative luminosity being 2.0 per cent for the 12 observers. This change is hardly greater than the estimated experimental error.

§ 9. FINAL RESULTS

The values of $K_{5780} : K_{5461}$ obtained by the sixteen observers, together with the Y/B ratio of each, are set out in table 4.

Table 4

Observer	Y/B ratio	K_{5780}/K_{5461} observed	Mean K_{5780}/K_{5461}
FMH	0.981	0.838, 0.854, 0.844	0.845
GEVL	1.030	0.896, 0.894	0.895
HB	1.052	0.897, 0.906	0.902
LHMcD	0.938	0.831, 0.855	0.843
WB	1.032	0.911, 0.964	0.938
JSP	0.963	0.872, 0.882	0.877
HFM	0.936	0.834	0.834
JWTW	1.039	0.910, 0.958	0.934
BHC	0.977	0.921, 0.867	0.894
THH	1.062	1.026, 0.974	1.000
FJCB	1.065	0.907, 0.951	0.929
HRS	0.979	0.863, 0.913	0.888
GCC	0.970	0.925, 0.912	0.919
CD	0.930	0.891, 0.838	0.865
GWGS	1.089	1.010, 0.984	0.997
BJO	1.010	0.874, 0.905	0.890
Mean	1.003		0.903

Colour temperature of comparison lamp, 2230° K. approximately; field-size of flicker photometer, 2°; field-brightness, 25 to 35 equivalent lux; an illuminated white surrounding field was employed in all cases. The photometer room was darkened.

§ 10. DISCUSSION OF RESULTS

Examination of the figures in column 3 of table 4 shows appreciable differences between the results obtained by the same observer on different occasions. These differences may be due to experimental error, to actual changes in the colour-sensitivity of the observer, or to both. The reproducibility of a single determination is assessed at $2\frac{1}{2}$ per cent, apart from any systematic error arising from the value used for $S_{5780} : S_{5461}$, so that in almost all cases the groups of figures in column 3 lie within the limits of error. This does not, however, necessarily exclude the possibility of changes in colour-sensitivity of individual observers.

In column 4 are given the individual mean values of $K_{5780} : K_{5461}$ and at the foot of the column the final mean value of 0.903. The value derived from the C.I.E. agreed curve is 0.899. The present results therefore show excellent agreement with

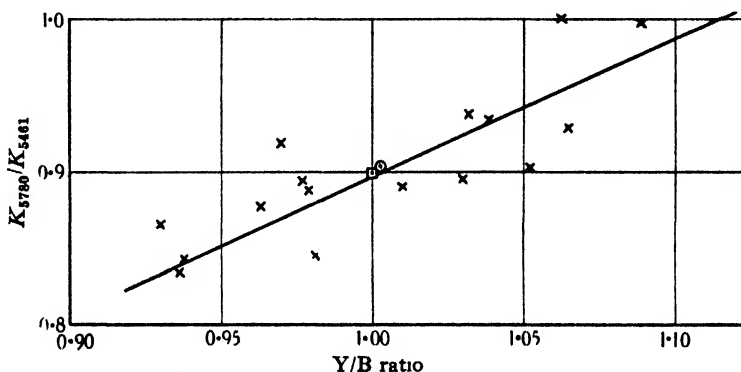


Figure 3. Relation between $K_{5780} : K_{5461}$ and the Y/B ratio. ⊙, centroid of observed values; ◻, C.I.E. standard eye; x, observed points.

the C.I.E. standard average eye, on the assumption that the mean readings of sixteen observers having a mean Y/B ratio of 1.003 are sufficiently representative.

If now the result of § 8 is used to reduce the mean observed value to a figure corresponding to the 1° field condition, the figure of 0.885 is obtained. This is in conflict with the inference to be drawn from the work of the other investigators mentioned, which is that a higher value of $K_{5780} : K_{5461}$ might be expected for the small-field condition.

A close systematic relationship between the quantity $K_{5780} : K_{5461}$ for each observer and his Y/B ratio is not necessarily to be expected. Figure 3 shows, however, that there is some such relationship when the results are considered as a whole. In this diagram individual mean values of the observed luminosity ratios are plotted against the Y/B ratios of the corresponding observers. The best straight line through the plotted points, obtained by the method of least squares, is also shown. The centroid of the experimental points and also the point corresponding to the C.I.E. standard observer are also plotted. These last two points lie close to each other and to the straight line which best represents the relationship between the two variables considered.

Further examination of this relationship is not within the scope of this paper, but it may be suggested here that it may possibly be explained on the basis of a bodily displacement of some definite luminosity curve towards shorter and longer wave-lengths, without change of shape.

It is next to be noted that the mean Y/B ratio of the sixteen observers employed, and chosen at random, was 1.003. Other workers in various countries have measured the Y/B ratios of larger groups of observers under similar experimental conditions and have obtained overall mean values very close to unity. This in itself is additional confirmation of the correctness of the standard luminosity curve as representative of the average human eye, since it is on the basis of the standard curve that the calculated total transmissions of the two filters employed in the Y/B ratio test have equal values.

§ 11. CONCLUSIONS

The results of the foregoing investigation may now be summarized thus:

(1) With the Guild flicker photometer, a 2° field, a field-brightness of 25 to 30 equivalent lux, a surround field of similar brightness and full eye-pupil in a dark photometer room, the mean value of $K_{5780} : K_{5461}$, i.e. (luminosity for 5780 Å.)/(luminosity for 5461 Å.) was found to be 0.90, for sixteen observers having a mean Y/B ratio of 1.003. This value agrees, within the limits of experimental error, with the ratio of 0.90 based on the C.I.E. standard luminosity values.

(2) Under the above conditions the field-size effect below 2° is detectable but small, and probably of the same order as the experimental error.

(3) The luminosity ratios for different observers show a general systematic relationship with their Y/B ratios.

The following results were incidental to the main investigation: (a) With suitable sector speeds no systematic errors due to stroboscopic effects were observed in the flicker photometry of intermittent light-sources of periodicity 100 c./sec. (b) The colour selectivity of a thermopile smoked with camphor black is negligible for the wave-length range considered. (c) Indirect support is lent to the correctness of the C.I.E. standard luminosity data by the fact that the mean Y/B ratio of the sixteen observers chosen at random was 1.003. A bodily shift of the standard C.I.E. curve as suggested by Arndt and Dresler (*loc. cit.*) in explanation of their results, would involve a change in this mean Y/B ratio to a value of approximately 1.10.

A more complete investigation, applied to a large number of lines distributed through the spectrum, is desirable and one has already been begun.

§ 12. ACKNOWLEDGEMENTS

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THE PURIFICATION AND MAGNETIC PROPERTIES OF MERCURY

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MS. received 7 February 1938

ABSTRACT. Differences between the magnetic properties of several specimens of mercury prepared by the Hulett method were removed by subsequently heating the mercury in vacuo at 260°C . for some time. The temperature variation of the mass susceptibility of mercury so treated was measured and the results are discussed with reference to a theory given by Stoner.

It is generally accepted that the best method of purifying mercury is that devised by Hulett⁽¹⁾ in which the metal, initially treated by the usual washing, high temperature distillation, and bubbling with air for many hours, is subsequently filtered and distilled in a stream of air at a pressure of about 2 cm. It is also generally assumed that mercury so prepared does not contain occluded gas, although Richards and Wilson⁽²⁾ reported that they had reason to fear that it contained a trace of oxygen; unfortunately, they gave no experimental evidence in support of their statement.

In the course of experiments⁽³⁾ on the magnetic properties of amalgams certain small differences were observed in the magnetic properties of mercury specimens which had been subjected to different temperature treatments, and were particularly noticeable in determinations of the temperature variation of mass susceptibility. It was therefore thought worth while to prepare mercury specimens by the Hulett method under different pressures of air during distillation and to find the mass susceptibilities of these specimens over the temperature range 16 to 300°C . The susceptibility-measurements were made by the Gouy method upon test specimens of mercury under the following conditions: (a) the mercury was placed in a degassed pyrex tube evacuated by means of a Hyvac pump and sealed; (b) the tube with the same mercury was again connected to the Hyvac pump and the liquid was boiled in a furnace maintained at 260°C . for 2 hr., after which the tube was sealed, one pyrex tube being used for as many specimens as possible to facilitate comparison.

In measurements following treatment (a), the curve of mass susceptibility against temperature always showed a discontinuity in the region of 140 to 180°C . In the case of specimens prepared in air at a pressure of 2 cm. or less, the diamagnetic susceptibility at room temperature for the (a) experiments was always less than that for the (b) experiments, and, even in the (a) experiments themselves, there

was a very slight increase in the room temperature value of the diamagnetic susceptibility after the specimen had been heated to 300° C. The nature of the discontinuity is shown in the figure.

One specimen was specially prepared in a stream of air at the relatively high pressure of 5 cm. and, while it showed a discontinuity at about 180° C., the values of the diamagnetic susceptibility at the lower temperatures in experiments (a) were definitely higher than those obtained in experiments (b), in marked contrast to the results with lower pressure preparations. The changes produced by boiling the mercury are small and rarely exceed 5 parts in 1000; it is difficult to follow them with precision. It is, however, strongly recommended, on the basis of the experiments described above, that mercury prepared by the Hulett method be subsequently boiled in an evacuated vessel before use.

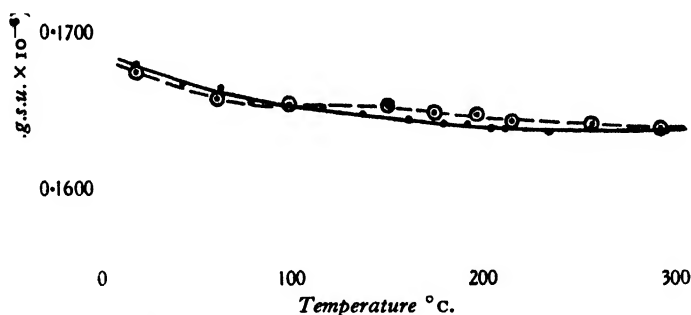


Figure 1. Mass susceptibility of mercury as a function of temperature; \odot , before boiling in vacuo; \bullet , after boiling in vacuo.

In the table are given the values of the mass susceptibility of mercury obtained with mercury distilled in air at a pressure of 2 cm. and later boiled in an evacuated tube; the absolute value at 20° C. is taken to be 0.1680×10^{-6} c.g.s. units per gram.

χ (c.g.s.u. $\times 10^{-6}$)	T (°C.)	χ (c.g.s.u. $\times 10^{-6}$)	T (°C.)	χ (c.g.s.u. $\times 10^{-6}$)	T (°C.)
0.1681	18.5	0.1653	110.5	0.1639	196.0
0.1668	42.0	0.1648	131.5	0.1639	203.5
0.1666	60.0	0.1644	154.0	0.1637	226.5
0.1656	75.0	0.1642	172.0	0.1640	247.5
0.1654	91.2	0.1641	184.5	0.1637	287.5

The temperature variation of the magnetic susceptibility of metals has been extensively discussed by Stoner⁽⁴⁾ and others. Stoner suggests that the increases in the paramagnetic susceptibilities of the alkali metals observed by Sucksmith⁽⁵⁾ are due to the change in the maximum energy of an electron in an energy band which for the present purpose may be taken as equal to that of a conduction electron at

absolute zero in Fermi-Dirac statistics, brought about by the expansion⁶ of the metals. He deduces that the quantity

$$\left[\frac{(\Delta\chi_A)_e}{(\chi_A)_e} \right] \Delta T$$

should be approximately equal to $\frac{2}{3}\alpha_v$, where $(\Delta\chi_A)_e$ is the change in the magnetic susceptibility $(\chi_A)_e$ of the conduction electrons in 1 gram-atom of metal for a temperature-rise ΔT , and α_v is the volume coefficient of expansion of the metal.

If we take 0.276×10^{-6} as a reasonable value⁽⁶⁾ for the diamagnetic susceptibility χ_a of the core of the mercury atom we have that the susceptibility of the electrons in 1 g. of mercury at 20° C. is

$$\{-0.168 - (-0.276)\} \times 10^{-6} = +0.108 \times 10^{-6} \text{ c.g.s. units.}$$

Now, the change in magnetic susceptibility as the temperature rises from 20 to 300° C. is 0.0043×10^{-6} . The calculated value of $\frac{2}{3}\alpha_v$ is therefore 0.000142 as compared with the experimental value of 0.00012; the agreement is striking, to say the least. However, the calculated value of $\frac{2}{3}\alpha_v$ is much affected by the value assumed for the magnetic susceptibility of the mercury core. Thus, if we take Shur's⁽⁷⁾ experimental value for the susceptibility of the mercury-vapour atom, viz. $-78 \pm 7 \times 10^{-6}$ c.g.s. units per gram-atom, as representing the diamagnetism of the core, we have

$$(\chi_A)_e = \{-0.168 - (-0.378)\} \times 10^{-6}$$

giving

$$(\Delta\chi_A)_e/(\chi_A)_e \cdot \Delta T = 0.000073,$$

and the agreement with Stoner's theory is not as good. Again, if we take Kido's⁽⁸⁾ experimental value -40.4×10^{-6} c.g.s. units per gram-ion for the Hg^{++} ion, as substantially the same for the mercury core, we get a calculated value for $\frac{2}{3}\alpha_v$ about four times too high.

It seems clear that the magnetic discontinuities described above cannot be attributed to occlusion of gases in the mercury. The quantity of occluded oxygen necessary to produce the observed changes is so considerable that in view of the doubts which have always been expressed with regard to suggestions that mercury occludes measurable quantities of oxygen or nitrogen, it is necessary to submit another reason for the discontinuities. It is suggested that, in the absence of a minute trace of gas, mercury atoms associate to form molecular groups with large electron-orbits such as have recently been postulated by Pauling⁽⁹⁾, by Lonsdale⁽¹⁰⁾, and by London⁽¹¹⁾ to explain the magnetic anisotropy of aromatic compounds, whereas the presence of gas would prevent such association. It is difficult perhaps to reconcile this picture with the fact that mercury distilled at the higher air pressure of 5 cm. was more diamagnetic in experiments (a) than in experiments (b), but it must be remembered that in this case the rate at which the mercury distilled was so great that the purity of the distillate may legitimately be suspect. Bailey, Fordham and Tyson⁽¹²⁾ have proved fairly conclusively that there is always a thin crystalline skin of some adventitious impurity upon the surface of mercury even though special precautions be taken to prevent its formation. It is difficult to see why the impurity

should be confined to the surface of the mercury alone, and we submit that the magnetic measurements prove that it is not. For on the contrary view we must presume the existence of a highly paramagnetic skin over the whole of the mercury in contact with the glass tube used in the magnetic experiments. However, the main purpose of this note is to draw attention to the fact that mercury purified by the Hulett method is more satisfactory for research purposes when it is subsequently heated in vacuo for some time.

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A NEW FORM OF FREQUENCY AND TIME STANDARD

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ABSTRACT. A description is given of a new form of quartz oscillator, designed to give a high frequency-stability under conditions of operation demanding little attention. It consists of a cylindrical quartz ring whose mean radius is about 2.7 cm., oscillating in an overtone longitudinal mode at a frequency of 100 kc./sec. The elastic wave round the circumference has six nodes, and the ring is supported at three of these nodes so as to be located with almost geometric precision with respect to the electrodes, with no constraints acting on it except those due to its own weight. Since the mean circumference of the ring remains unchanged during the vibration there is little air damping, and strong oscillations are obtained at atmospheric pressures. The temperature coefficient of frequency depends on the difference between the internal and external radii of the ring and can be reduced to zero at a particular temperature, the average coefficient being less than 1 part in 10^6 per 1°C . for temperatures 15°C . above and below that value. The frequency-stabilities of two equipments are given. An oscillator at room-temperature and atmospheric pressure, and not maintained in continuous operation, gives a stability of ± 5 parts in 10^9 during periods of an hour, and ± 1 part in 10^7 during weekly periods. An oscillator maintained in continuous operation in an evacuated container at a controlled temperature, and used as a standard of time, gives a stability of ± 4 parts in 10^{10} during hourly periods, and 1 part in 10^8 during monthly periods.

§ 1. INTRODUCTION

THE quartz resonator was first used as a standard of frequency by Professor Cady in 1922, and it was some time after this that the resonator was successfully incorporated in a valve oscillatory circuit to control the frequency of electrical oscillations. Such rapid progress has been made in this field, however, that now the quartz oscillator not only is widely used for stabilizing the frequency of transmitting stations but also constitutes the most accurate means of recording the passage of time. The highest long-period frequency-stability attainable by the ordinary quartz plates used for controlling the frequency of transmitting stations is of the order of several parts in 10^6 , and that attainable by the best quartz frequency and time standards is 1 part in 10^8 . There is still a definite need for an oscillator which gives a stability considerably better than 1 part in 10^6 and is yet reasonably inexpensive, robust, portable, and calls for little maintenance attention.

The main purpose of the work described in the present paper is the development of such an oscillator. Its successful accomplishment, however, automatically provides the basis for a new form of primary standard, for an oscillator that maintains a frequency stability better than 1 part in 10^6 , when operating under

conditions of no particular refinement and with little attention, should give a stability at least as high as any yet attained, when operating under more constant and favourable conditions. An oscillator of the type described has been installed in a manner appropriate for a primary standard and is now in operation as the National Physical Laboratory quartz clock no. 2. A short description of the equipment is included in the paper, together with the results so far obtained.

§ 2. STATEMENT OF THE PROBLEM

It is the author's experience that the frequency-stability of quartz-controlled oscillations depends more on the quartz itself and the manner in which it is supported than on the circuit. It is true that the performance of a poor oscillator may often be improved by modifications of the driving circuit, but if the quartz is suitably mounted so as to have a very low logarithmic decrement, of the order of 10^{-5} , the frequency of oscillation is so little dependent on the circuit conditions that the simplest circuit is quite satisfactory and any risk of trouble arising from unnecessary elaborations is avoided. The investigation was, therefore, confined almost entirely to the quartz and its mounting, and the circuit used differs little from that of the quartz standard already in use at the National Physical Laboratory⁽¹⁾.

As a guide to the development of the new form of quartz oscillator the following particular requirements, regarded as desirable, may be enumerated. (a) The temperature coefficient of frequency should be less than 5 parts in 10^7 per 1°C . so that only a rough form of temperature-control is required. (b) The quartz and the electrodes must be precisely and permanently located with respect to one another. The frequency variation that may be caused by varying the gap between the quartz and the electrodes is of the order of 2 parts in 10^3 , and it is therefore evident that the greatest possible precautions must be taken to prevent any relative displacements. In the first place the quartz should be symmetrically disposed between the electrodes so that the effects due to movement of the quartz tend to compensate, and secondly the quartz and electrodes should be rigidly located. The location should be invariable with temperature, pressure, external vibration and time. (c) The location should be effected in such a manner that the quartz can be easily removed and replaced in exactly the same position. This greatly facilitates the adjustment of the quartz to an exact frequency. (d) It is desirable that the oscillator should be capable of operating at atmospheric pressures, as this also considerably facilitates the frequency-adjustment. (e) It should be possible to adjust the frequency of vibration to within a few parts in 10^6 of the required value by altering the dimensions of the quartz, for if the frequency is suitably independent of external conditions, such as temperature, little adjustment can be made by altering these conditions. A small final adjustment can, however, be effected by the insertion of a suitable capacitance across the quartz electrodes. (f) The variations of frequency with the circuit conditions and the supply voltages should be so small that these do not require any close control. (g) There should be no appreciable drift in frequency after the switching-on of the voltage supplies to the oscillator. It is

clearly inconvenient for many purposes if the oscillator needs to be in continuous operation to give a known, steady value of frequency.

It might be thought that an oscillator similar to the best quartz standards at present in use, but made in a somewhat cheaper, less elaborate form, would fulfil the above conditions, but a consideration of their design shows that this is not the case. The standards that, according to published results, have so far given the best performances, are those installed at the Physikalisch-Technische Reichsanstalt⁽²⁾ and the National Physical Laboratory⁽¹⁾.

Those at the former institute consist of quartz bars about 9 cm. long held at the nodes by silk or wire threads and mounted in evacuated glass tubes. Two types are used, one having a temperature coefficient of about -3 parts in 10^6 per 1°C. , and the other, later, type a few parts in 10^6 per 1°C. at a particular temperature. Although these possess many desirable characteristics it seems that it is very difficult to adjust the frequency to a precise value, for most of the oscillators of this form reported on differ from their nominal value by several parts in 10^5 .

The standard at the National Physical Laboratory consists of a quartz ring of diameter approximately 10 cm., suspended between the electrodes by means of three fine wire stirrups. It operates in an evacuated glass vessel, and its temperature coefficient is about -2.5 parts in 10^6 per 1°C. The large size of this ring, its rather high temperature coefficient, and the fact that its level must be carefully preserved, make it quite unsuitable for standards of the type here considered.

§ 3. THE NEW FORM OF OSCILLATOR

A number of preliminary experiments were carried out with bars and rings of quartz and with different systems of mounting, and the form now described was chosen as most nearly fulfilling the requirements enumerated in the previous section. A very brief description of it was given in a letter published in *Nature*⁽³⁾ in 1935.

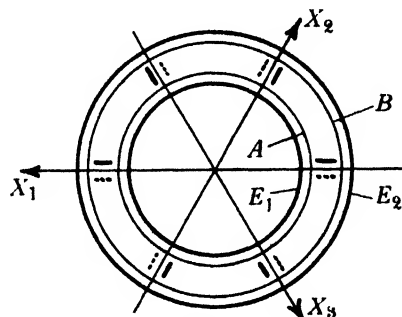


Figure 1.

It consists of a hollow cylindrical quartz ring whose axis is in the direction of the optic axis of the crystal. The two electrodes are coaxial metal rings E_1 , E_2 , figure 1, at a distance of about 2 mm. inside and outside the cylindrical surfaces of the quartz. There are three electric axes X_1 , X_2 , X_3 in the plane of the ring. An

electric field across the electrodes therefore produces, by virtue of the converse piezoelectric effect, circumferential strains which vary in amplitude round the ring and are of opposite sign at points 60° apart. An alternating electric field produces alternating circumferential strains which are of opposite phase at these points. When the frequency of the applied alternating field equals the appropriate natural frequency of the quartz ring, a strong longitudinal, compressional vibration round the circumference of the ring is excited, and considerations of symmetry indicate that the vibration of this kind of lowest frequency is one having nodes at the six sectional areas where the planes containing the electric axes and the cylindrical axis cut the ring. This overtone longitudinal vibration having six nodes and three complete waves round the circumference is the one used in the new form of oscillator. The mean circumference remains constant during the vibration, so that there is no deformation of the ring except periodic changes in the cross-sectional dimensions, which vary in phase and amplitude round the circumference.

The frequency of vibrations of this kind in a ring of small circular cross-section is given by the formula⁽⁴⁾

$$N = \frac{\sqrt{(1+S^2)}}{2\pi} \cdot \frac{q}{a\rho} \text{ c./sec.}$$

in which q is the Young's modulus, ρ the density, a the mean radius, and S the number of waves round the circumference. Inserting the appropriate values for quartz, $q = 7.85 \times 10^{11}$, $\rho = 2.65$ and taking S equal to 3, we have

$$N = \frac{2.735}{a} \times 10^5 \text{ c./sec.}$$

Since the rings actually used are of approximately square section, the sectional dimensions being comparable with the mean radius, the above formula would not be expected to apply exactly. An empirical formula obtained from measurements of a number of rings is

$$N = \frac{2.67}{a} \times 10^5 \text{ c./sec.}$$

The frequency, depending only on the mean radius, can be adjusted in either direction by grinding the inside or outside cylindrical surface as the case may be. The fineness of adjustment is such that it is necessary to grind with an abrasive powder for several minutes to change the frequency by 1 part in 10^5 . The frequency of 100 kc./sec. was chosen as being the most suitable from several different considerations. It gives a ring of convenient size, the mean radius being 2.67 cm. It enables the ready control of multivibrators at frequencies of 1, 10, 100, and 1000 kc./sec., which are almost universally employed in modern methods of frequency measurement, and if the ring is to be used for controlling the frequency of a transmitter, not many stages of frequency-doubling would usually be required to derive the transmitter frequency from a frequency of the order of 100 kc./sec.

§ 4. THE ELECTRODES AND METHOD OF MOUNTING

An assembly drawing of the quartz ring and electrodes is shown in figure 2. The internal electrode 1 is cut from a solid brass rod, so that three arms 2 spaced at 120° are left projecting. The arms carry chisel-ended phosphor-bronze screws 3 whose chisel ends are thinned down to a thickness of about 0.25 mm., rounded, and polished. These polished ends are located in V-shaped grooves, 0.25 mm. deep, cut radially in the lower face of the quartz at three nodal positions. The quartz is thus located with respect to the electrode with almost geometric precision and is yet under no restraints except those arising from its own weight. The outer electrode 4

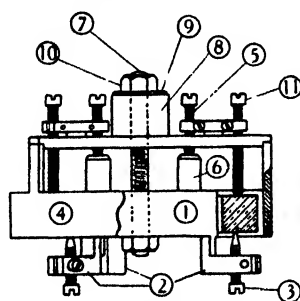


Figure 2.

is located in a similar manner with respect to the inner electrode. Three screws 5 with rounded and polished ends, and carried by a spider fixed to the electrode, fit into V-shaped grooves cut radially in the fused-quartz pillars 6, which are fixed in the inner electrode. The three units of the oscillator are thus very precisely located and can be taken apart and reassembled without the relative positions being changed. In order to make the system completely portable, the two electrodes are held in position by means of the brass bolt 7, fused-quartz insulating tube 8, brass cap 9, and nut 10; and the screws 11, with rounded and polished ends, are screwed down and locked at a distance of 0.01 mm. from the upper surface of the quartz ring, so that though they do not constrain it in any way, they prevent the bottom locating screws from leaving the grooves in the ring.

§ 5. LOCATION OF THE NODAL POINTS

It was expected that the nodes of vibration would approximate to the areas where the planes containing the electric axes X_1 , X_2 , X_3 , figure 1, and the cylindrical axis cut the ring. The experimental investigation was limited to the determination of the nodal points on the two plane surfaces of the ring. For this purpose the ring was supported between the electrodes on three metal balls spaced symmetrically round its mean circumference, and it was rotated on these in the direction of the circumference until it oscillated with maximum amplitude. The three points of contact were then assumed to be three of the six nodal points. The next position for maximum amplitude determined the other three nodal points. The ring was then turned over and the six nodal points on the other surface were determined.

These positions were easily located with an accuracy of 1° of rotation. They are shown in figure 1 as full lines for the nodes on the top surface of the quartz and broken lines for those on the under surface. It is seen that the nodes on the two surfaces lie in planes inclined at considerable angles to those formed by the electric and cylindrical axes, and that these inclinations are of opposite senses for neighbouring pairs of nodes. The value of the angle of inclination for the four rings whose dimensions are given in table 1 is 35° . This means that for rings of a thickness of 1 cm. in the direction of the optic axis, the nodal points on the front surface, as viewed in figure 1, are displaced by 3.5 mm. in a clockwise direction from the electric axes, and those on the back surface are displaced by the same amount in an anti-clockwise direction.

Table 1

Quartz ring no.	Outer diameter (mm.)	Inner diameter (mm.)	Mean diameter (mm.)	Width (mm.)	Thickness in direction of optic axis (mm.)	Temperature at which temperature coefficient is zero ($^\circ$ C.)	Frequency (kc./sec.)
3	62.4	43.0	52.7	9.68	11.3	55.0	100.00
	62.35	43.5	52.92	9.42	11.3	50.5	100.00
	62.3	43.6	52.95	9.33	11.3	49.0	100.00
	62.15	44.15	53.15	9.00	11.3	45.0	100.00
	61.4	46.8	54.1	7.3	10.7	23.0	100.00
	61.32	46.8	54.06	7.26	10.7	22.0	100.00
4	61.77	44.95	53.36	8.41	10.0	44.0	100.00
	61.70	45.18	53.45	8.26	10.0	42.0	100.00
	61.68	45.18	53.43	8.24	10.0	40.0	100.00
	61.60	45.18	53.39	8.21	10.0	38.0	100.00
2	62.2	43.36	52.78	9.42	11.05	54.0	100.00
	61.44	45.22	53.33	8.11	11.05	25.0	100.00
5	61.70	44.5	53.10	8.6	10.9	31.0	99.27

The inclination of the nodal plane is probably an effect analogous to that described by Straubel⁽⁵⁾ and may be attributed to the difference between the elastic coefficients measured in different directions of the quartz crystal.

The directions of the electric axes were found by applying a mechanical pressure to the cylindrical surfaces at points such as *A*, *B*, all round the ring, and measuring the potential-difference developed as a result of the piezoelectric effect. Maximum potentials are obtained at the points where the electric axes are radial to the ring, and when the potential is negative on the outer surface the direction of the axis is from the centre towards the circumference.

§ 6. TEMPERATURE COEFFICIENT

The temperature coefficient of frequency of the rings depends on the difference between the internal and external radii and on the temperature. The relationship was investigated experimentally by gradually reducing the width of a ring and determining the {frequency, temperature} curve at a number of different values.

A ring of width 10 mm. was cut, and adjusted to have a frequency of 100 kc./sec. The width was reduced by grinding the two cylindrical surfaces by amounts such as to keep the frequency at 100 kc./sec. Figure 3a shows the variations of frequency with temperature at one particular width, and figure 3b gives the relationship between the width of the ring and the temperature at which the temperature coefficient is zero.

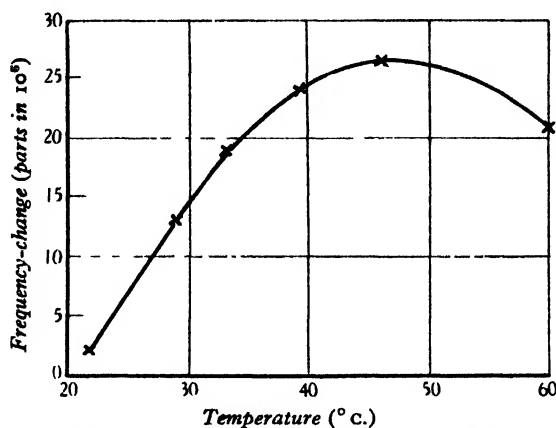


Figure 3a. Variation of frequency with temperature.

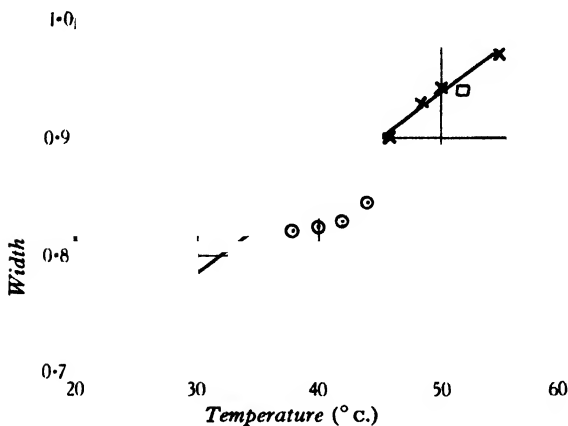


Figure 3b. Variation of maximum of temperature curve with the width of the ring.
x, ring 3; ⊙, ring 4; □, ring 2.

When the width was reduced below 9.0 mm., for which value the zero coefficient was obtained at 46° C., the oscillations of the ring became rapidly weaker. It was tested as a resonator and found to resonate feebly at a frequency of about 101 kc./sec., as well as at 100 kc./sec. As the width was further decreased, the resonance at 101 kc./sec. became stronger and the one at 100 kc./sec. weaker, and when the ring finally oscillated again it did so at a frequency of 101 kc./sec. A considerable adjustment was obviously now necessary, and was made by grinding the inside surface only to bring the frequency back to 100 kc./sec. When this was done the width was 7.3 mm. and the zero coefficient was at 23° C. The history and dimensions

of this ring, designated as quartz ring no. 3, are shown in table 1. Another ring, quartz ring no. 4, was tested repeatedly as a resonator, and as soon as the second resonance could be detected, the frequency of this resonance was adjusted to be 100 kc./sec. It then oscillated strongly in this mode when the thickness was 8.41 mm. and the zero coefficient was at 44° C. Quartz ring no. 2 behaved in a similar manner and was satisfactorily adjusted to have a zero coefficient at 25° C. Quartz ring no. 5 behaved somewhat differently, the second mode being only 0.5 kc./sec. removed from the first mode, but it was satisfactorily adjusted to have a zero coefficient at 31° C. Its frequency was adjusted to 99.27105 kc./sec. as the ring was intended to serve as a sidereal time standard at an observatory. A demultiplication factor of 99,000 gives a frequency of 1.0027379 per mean solar second, or 1.0000000 per sidereal second.

The experience obtained with these four rings shows that 100-kc./sec. oscillators can be made with a zero temperature coefficient at any temperature in the ordinary working range, but that if, as is usually the case, the actual value of the temperature of operation is not important, it is best to adjust the rings to have a zero coefficient in the region 50° C. to 60° C. as no trouble is then experienced with the second resonance. It appears from the close agreement of the dimensions of the different rings that it should be possible to cut a ring to have a frequency within a few parts in a thousand of the required value, with a zero coefficient at a temperature between 50° C. and 60° C.

§ 7. THE ELECTRICAL CIRCUITS

The electrical circuits do not differ in principle from those described by the author in an earlier paper, and it is not thought necessary to give detailed descriptions or diagrams. The Pierce circuit is used for maintaining the quartz in oscillation, and this is followed by a single buffer stage from which the output at 100 kc./sec. is taken. One difference which may be noted is the introduction of a condenser connected across the electrodes of the oscillator. This is a specially designed quartz insulation micrometer condenser which enables the frequency to be changed by a total amount of ± 5 parts in 10^6 , and by 4 parts in 10^9 per scale division. Another new feature is the use of toroidal coils in the driving and buffer circuits. This is found to result in a considerable reduction in the effect of fluctuations of the supply voltages on frequency, possibly owing to the more complete decoupling between the two stages.

For the purpose of measuring the frequency directly in terms of astronomical time signals, an output at the frequency of 100 kc./sec. controls two multivibrators in cascade at frequencies of 10 kc./sec. and 1 kc./sec. respectively. An amplified output at 1 kc./sec. drives a phonic motor from which impulses at 1.0 sec., 0.1 sec. and 0.01 sec. can be obtained, for recording on a chronograph together with the time signals.

§ 8. PERFORMANCE

Frequency variations with changes in circuit conditions. It is obviously desirable to have the fullest information concerning the dependence of frequency on the

circuit conditions, and detailed measurements were made. The results are given in a very condensed form in table 2 to show the degree of stability attained.

Table 2

10 per cent increase of	Frequency-change (parts in 10^6)
Anode voltage	+ 1
Filament voltage	+ 3
Conductance between electrodes	- 4
Value of LC in tuned circuit in anode of driving valve	+ 6
Grid-filament capacitance of driving valve	- 200
Grid-anode capacitance of driving valve	- 200

The effect of coupling an output coil to the anode coil of the driving valve is a change of frequency of about 1 in 10^7 , but there is no measurable change when the output is taken from the buffer valve. The curve showing the variation of frequency with temperature has already been given in figure 3a. Similar curves were obtained for all the rings tested, the only difference being the temperature at which the coefficient was zero. The total change of frequency as the pressure is reduced from 760 mm. to 0 mm. of mercury is of the order of 4 parts in 10^6 , but the pressure coefficient in the region of atmospheric pressure is only about 0.02 part in 10^6 for a change of pressure of 100 mm. of mercury.

The logarithmic decrement of the oscillator is 6×10^{-5} in air and 3×10^{-5} in vacuo. If the oscillator is shaken, or knocked with sufficient violence to make the quartz jump on its supports, frequency changes of as much as one or two parts in 10^7 sometimes occur, but ordinary vibrations of the room such as might be caused by motor generators have no measurable effect. A light spring pressure applied at three of the nodes on the upper surface of the quartz causes the frequency to be completely unaffected by knocking or shaking, but the pressure itself causes a frequency change of a few parts in 10^6 . It is obvious that changes of this pressure could produce quite appreciable variations of frequency, and in the author's opinion the unclamped type is more satisfactory for most purposes. The oscillators whose performances are discussed here are of this type.

Frequency-stability. In view of the twofold object of this work—the production of a simple, robust, standard of frequency, and the incorporation of this in a primary frequency and time standard—the frequency-stability of the oscillator with respect to lapse of time will be considered when it is operating under two different sets of conditions. In the first case an oscillator whose zero temperature coefficient was in the neighbourhood of room-temperature (quartz ring no. 3, table 1) was mounted in a metal pot, which was filled with dry air and then sealed with a rubber gasket. This precaution was to protect the crystal from changes of humidity rather than of pressure. The oscillations were maintained by the simple Pierce circuit, and the voltage supplies obtained from general utility batteries, which were subject to variations in voltage of ± 10 per cent. The oscillator stood on a pad of felt on an ordinary laboratory table in a room where the temperature-

variations amounted to $\pm 1^\circ \text{C}$. The temperature of the oscillator was not controlled but followed the variations of the ambient temperature of the room. The frequency was measured at intervals during a period of several months, the voltage supplies to the oscillator being switched on a few minutes before the measurements were made. It was found that the drift after switching on was no more than 1 part in 10^8 , that the frequency-variations during an hour were of the order of $\pm 0.5 \times 10^{-8}$, and that the stability over a period of a week was of the order of $\pm 10 \times 10^{-8}$. There was, however, a slow drift in frequency of about +10 parts in 10^8 per week, which so far has not been explained. This is not regarded as a very serious drawback in a substandard of frequency, since it can be checked periodically by comparison with standard frequency emissions and any necessary adjustment can be made. The important characteristic is the high degree of stability attained when the crystal is operating under conditions demanding little attention.

The other stability-measurements relate to an oscillator installed as a primary standard. Quartz ring no. 2, table 1, was sealed in an evacuated fused-quartz container and housed in an oven controlled to within $\pm 0.01^\circ \text{C}$. at the temperature at which its temperature coefficient is a minimum. The driving, demultiplying, and amplifying circuits were operated by trickle-charged batteries, and the equipment was maintained in continuous operation as quartz clock no. 2. Outputs at frequencies of 100 kc./sec. and 1 kc./sec. were available for purposes of frequency-measurement, and 1-second contacts on the phonic motor were used for comparing the rate of the standard with other time standards and with astronomical signals.

The short-period stability of frequency was determined by combining the 100-kc./sec. outputs of two similar, but entirely independent, oscillators and measuring the period of the beat obtained. Continuous measurements were made for one hour, each measurement being of about 200 seconds' duration. No departures of more than 4 parts in 10^{10} from the mean value of their frequency-difference were observed.

The mean daily rate of the clock was measured by recording the seconds impulses from the phonic motor and the time signals from Paris, Rugby and Hamburg, on a chronograph. The rate averaged over 10 days and for the three sets

Table 3

Date, 1937	Mean daily rate (sec./day) obtained from corrected time signals			
	Paris	Rugby	Hamburg	Mean
March 3 to 13	-0.020	-0.021	-0.019	-0.020
March 13 to 19	-0.021	-0.018	-0.022	-0.020
April 8 to 18	-0.020	-0.020	-0.016	-0.019
April 18 to 28	-0.019	-0.020	-0.023	-0.021
April 28 to May 8	-0.020	-0.021	-0.019	-0.020
May 8 to 13	-0.017	-0.020	-0.021	-0.019
May 16 to 26	-0.016	-0.017	-0.018	-0.017
May 26 to June 5	-0.018	-0.014	-0.017	-0.016
June 5 to 15	-0.015	-0.018	-0.015	-0.016
June 15 to 25	-0.014	-0.019	-0.018	-0.017

of time signals was usually accurate to ± 0.001 sec. per day, when the corrections to the signals had been applied. Although the oscillator has been in continuous operation since March, 1937, it has not been possible to obtain a complete record of its rate, owing to a modification to some of the associated equipment, but the results obtained in table 3 indicate that the performance is as good as that of any clock so far installed.

Although there is again a gradual increase in the frequency of the standard, this is now so small and uniform, that accurate allowance can be made for it when the present rate of the clock is calculated. The latter can be predetermined with a precision of ± 0.001 sec./day, or 1 part in 10^8 .

§ 9. ACKNOWLEDGEMENTS

In conclusion the author wishes to express his appreciation of helpful discussion with his colleagues, in particular Dr L. Hartshorn and Dr G. A. Tomlinson; and also of the interest with which the work has been followed by the superintendent of the Electricity Department, Dr E. H. Rayner.

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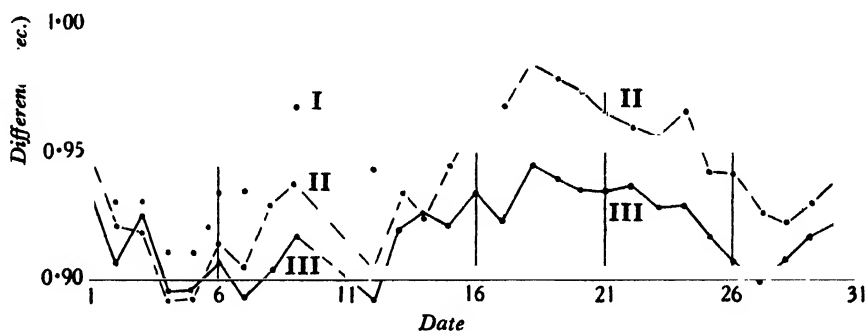
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DISCUSSION

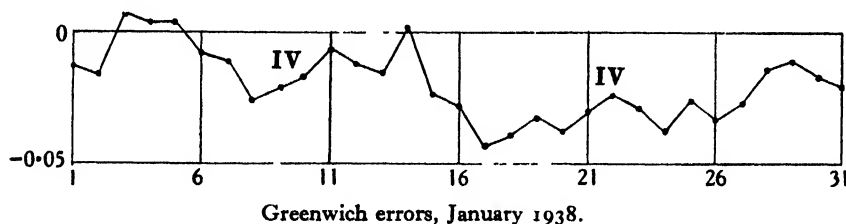
Mr E. C. ATKINSON. When the quartz crystal was first used as a clock, the frequency was by no means independent of the working conditions—valve, voltage, temperature and pressure. The author has shown how these interferences have been reduced, notably by arranging to work at a temperature for which the rate is a maximum. He has made an engineer's job of the construction. I am interested in the crystal mainly as a primary standard, and I am looking forward to the time when it will assist in the time service at Greenwich. My clocks are compared with the Greenwich signals and, in the middle of February, I sent a chart to the observatory showing the comparison of my E_{15} with the 10.0-h. rhythmic signal from Rugby for the previous 50 days, before the corrections to this signal for January had been published. These corrections are arrived at after balancing possible irregularities in clock-rates against possible errors in transit determinations of time. The crystal clock will not reduce errors in star observations, but it may assist in estimating their values, for with a perfect clock they would be exactly known. Curve II, corrected for stratification, shows that E_{15} was fast on the Rugby signal between 0.89 sec. and 0.98 sec., a range of 0.09 sec. during January. The Greenwich errors, IV, account for part of this, reducing the range to 0.05 sec. The corrected curve III, except for

the last few days of the month, is similar in general shape to a reflection of the Greenwich chart. A single clock cannot give reliable information about Greenwich errors, but the reflection appearance can be explained on the assumption that the errors are in general greater than those found from the Observatory data, with a range about half as large again.

1.05



Extent to which E_{15} is fast on Rugby 10.0-h. rhythmic signal. I, as observed; II, reduced to 2.3°F . stratification, range 0.092 sec; III, corrected for Greenwich errors, range 0.052 sec.



Dr D. OWEN. It is astonishing to learn of the construction of a clock based on the action of a quartz ring oscillating with a frequency of 100,000 c./sec., and to have evidence that it maintains its uniformity within a margin as small as four parts in 10,000 millions, at least for short periods of about an hour. Such constancy appears amply to exceed anything claimed for the Shortt pendulum clock, and this latest type of quartz time-keeper appears to have the further advantage of being independent of gravity. The problem of the degree of uniformity of the earth's rotation would seem to be now within range of definite solution.

Mr D. A. BELL. I believe the advantages of the circular quartz oscillator arise from the absence of faces having large displacements normal to the surface, and the existence of well defined nodes; these features minimize air damping and the effect of supports on the frequency of the oscillator. The shape in question has also the advantage that frequency is little affected by small displacements of the electrodes. The temperature coefficient of frequency of the quartz ring alone can therefore be

made zero, without the need for any allowance for the effect of temperature* on the electrode system. The obvious disadvantage, however, is the need for such large volumes of quartz, which must be free from both optical and electrical twinning.

With regard to the very high stability of frequency observed, the figure of 4 parts in 10^{10} for one hour corresponds to a change in phase-difference between two 100-kc./sec. oscillators of about 0.01 cycle at the end of the hour. If the two oscillators compared are of identical quartz-ring construction, is there not a risk of undetected drift of both in the same direction, due to a specific property of this type of oscillator, such as internal heating?

I should be interested to know the sign of the change of frequency with damping, for I wonder whether the extremely small but persistent change given in table 3 (about 3 parts in 10^8 after 4 months) may not be due to a slight change in damping at any part of the system.

Has the thickness of the ring in the direction of the optic axis any influence on the ratio of outer to inner diameter for a given thermal performance? I notice that ring no. 3, 11.3 mm. thick, gave a zero temperature coefficient at 45° C. with a ratio of about 1.41, but ring no. 4, only 10 mm. thick, for 44° C. had a ratio of about 1.37. On the other hand, ring 2 and ring 3, nearly equal in thickness, have ratios of about 1.44 and 1.45 for 54° C. and 55° C. respectively. I should also like to ask whether the thickness has any effect on the second resonance, since the presence of this undesired frequency would be one of the chief difficulties in the manufacture of such oscillators.

Dr F. J. W. WHIPPLE. The author points out that Hoppe's formula for the frequency of vibration of a ring* is not quite consistent with observation; the discrepancy is about 2 per cent. It is worth noticing that Hoppe's formula allows for the radial component in the oscillation, though this component would probably be of less importance in a substantial ring than in the thin one for which the formula is proved. If the radial component were ignored entirely, S would have to be substituted for $\sqrt{(1+S^2)}$ in the formula. Since $\sqrt{10}:3$ is equal to 100:95, this would imply a reduction of 5 per cent in the calculated frequency; the observed reduction of 2 per cent might well have been anticipated.

AUTHOR'S REPLY. The main purpose of the quartz clocks is, as Mr Atkinson remarks, to smooth out the errors of time-determination during intervals in which no stellar observations are possible. Whether they are more stable over long periods than pendulum clocks is still to be determined, but their present advantages are that they do not appear to be subject to sudden changes of rate, and that a number of such clocks can be intercompared with great accuracy. The time given by a group of three such clocks would be expected to have a very high day-to-day uniformity, and stellar observations need only be used to correct for any gradual departure from the true sidereal time.

It does seem possible, as Dr Owen suggests, that such a group of clocks might be able to reveal changes in the period of the earth's rotation.

* The proof is given in Love's *Treatise on Elasticity*, 2, 183 (1893).

Mr Bell points out that two such clocks might drift in the same direction without the fact being discovered by their intercomparison. This is of course possible, but it is unlikely to happen when the two equipments are completely separate. The probability is still less if the standards are of different types, and I have in fact made check measurements using the present standard, the Dye quartz oscillator, and a quartz bar. The effect of damping on frequency depends, I think, on the nature of the damping. A general loading, such as that due to air or moisture, would probably cause a decrease in frequency, but it is known that an applied mechanical pressure causes an increase in frequency. I think it is very difficult to attribute to any specific cause the small change in frequency that has so far occurred. A few experiments were made to find whether the thickness of the ring affected its performance, and from these it was concluded that between the values of 11.5 mm. and 7 mm. it has little effect as regards either the conditions for zero temperature coefficient or the second mode of oscillation.

Dr Whipple's suggestion appears to be a useful one, but I should not like to comment on it without looking further into the derivation of Hoppe's formula.

A ROTATIONAL ANALYSIS OF BANDS OF LEAD SULPHIDE

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ABSTRACT. A rotational analysis has been made of the (6, 0), (7, 0), (9, 0), (2, 1), (3, 1) and (4, 1) bands of the $\Lambda \leftarrow X$ system of lead sulphide as observed in absorption. The structure of the bands is that which would be given by a $^1\Sigma \leftarrow ^1\Sigma$ transition. A least-squares fit of the B' values obtained gives $B_v' = 0.08560 - 29.55 \times 10^{-5} (v' + \frac{1}{2})$ cm.⁻¹ whilst $B_0'' = 0.105614$ cm.⁻¹ and $B_1'' = 0.104741$ cm.⁻¹ Other constants determined were $D_0'' = -2.573 \times 10^{-8}$ cm.⁻¹, $D_0' = -2.508 \times 10^{-8}$ cm.⁻¹, $r_e'' = 0.7552$ Å. and $r_e' = 0.8406$ Å. The bands analysed were due to ²⁰⁸PbS, whilst a considerable number of lines observed were accounted for as due to ²⁰⁶PbS and ²⁰⁷PbS.

§ 1. INTRODUCTION

THE band spectrum of lead sulphide was first observed by Rochester and Howell⁽¹⁾. The absorption spectrum of this molecule, as observed by them, stretched from $\lambda 3100$ to $\lambda 8500$ and consisted of overlapping progressions of bands degraded to the red. Five systems were recognized; these had a common ground state and were represented by the following equations:

$$\left. \begin{aligned} \text{System A: } \nu &= 18,851.3 + 261.09 (v' + \tfrac{1}{2}) - 0.365 (v' + \tfrac{1}{2})^2 \\ \text{,, } B: \nu &= 21,847.7 + 282.17 (v' + \tfrac{1}{2}) - 0.856 (v' + \tfrac{1}{2})^2 \\ \text{,, } C: \nu &= 23,212.9 + 303.93 (v' + \tfrac{1}{2}) - 1.436 (v' + \tfrac{1}{2})^2 \\ \text{,, } D: \nu &= 25,024.4 + 283.95 (v' + \tfrac{1}{2}) - 1.171 (v' + \tfrac{1}{2})^2 \\ \text{,, } E: \nu &= 29,650.5 + 299.34 (v' + \tfrac{1}{2}) - 1.574 (v' + \tfrac{1}{2})^2 \end{aligned} \right\} \begin{aligned} & \\ & \\ & - 428.14 (v'' + \tfrac{1}{2}) \\ & + 1.201 (v'' + \tfrac{1}{2})^2. \end{aligned}$$

In passing, it is of interest to note that there is a quite definite parallelism between the structure of the spectrum of lead sulphide and that of plumbic oxide.

§ 2. EXPERIMENTAL DETAILS

The lead sulphide vapour was obtained by heating lead sulphide in a vitreosil or alundum tube surrounded by a wider iron tube, the composite tube being placed in an electric furnace having Silit rod heating elements. The internal diameter of the inner tube was 3.8 cm. and the furnace length was 30 cm. The temperature employed ranged from 800° to 1000° C. Actually, of course, only the middle portion of the tube (probably some 8 cm.) was at the temperatures quoted. The composite

tube was employed for the sole reason that the absorption tubes had to be as thick-walled as possible because of the destructive action of lead sulphide on all the materials available, vitreosil, alundum, and glazed and unglazed porcelain. However, the outer metal tube also was of use in that its higher conductivity would help to lengthen the heated column.

The spectrograms were obtained in all orders from the first to the fourth of the 21-ft. Rowland grating in the University of Manchester Physics Department. This grating is now in a Paschen mounting⁽²⁾ which is extremely suitable for the type of work under consideration, in that a number of spectrograms can be obtained simultaneously, in different orders if necessary. The iron arc was used throughout as a comparison spectrum.

§3. ANALYSIS

Owing partly to the complexity of the spectrum and partly to the temperature found necessary to give reasonable absorption it has only been possible to analyse six bands out of the 230 listed by Rochester and Howell. The bands analysed belong to the A system (i.e. A ← X), and table 1 gives the data for them. It will be seen that three of the bands, namely (6, 0), (8, 0) and (9, 0), arise in the ground state (X, $v''=0$) and the other three, namely (2, 1), (3, 1) and (4, 1), in the first excited level of this ground state. The group with v'' equal to 0 were photographed in the fourth order of the grating and the others in the second order. These bands were fairly easily resolved into *P* and *R* branches, with the exception of (4, 1), in which the two branches coincide. No evidence for a *Q* branch was found, but since, as the analysis shows, the origin is close to the head (where the lines could not be separated) it is not impossible that a short *Q* branch exists. However, on the evidence available it seems probable that the spectrum is due to a ${}^1\Sigma \leftarrow {}^1\Sigma$ transition.

Analysis depends on the theoretical formula

$$R(J-1) - P(J+1) = 4B''(J + \frac{1}{2}) + 8D''(J + \frac{1}{2})^2 \quad \dots\dots(1),$$

where

$$D'' = -4B''^3/\omega^2 \quad \dots\dots(2),$$

the symbols having their usual significance.

The bands (8, 0) and (9, 0) were measured first, and it was found impossible to decide which was the better of two arrangements of (*R* - *P*) differences, for each gave nearly identical values in both bands. However, on measurement of (6, 0) it was at once possible to decide between the alternatives.

Although the above procedure gave us lines having corresponding values of *J* it did not determine the absolute values of the *J*s, and this proved to be the main difficulty of the analysis. On rewriting equation (1) in the form

$$\{R(J-1) - P(J+1)\}/(J + \frac{1}{2}) = 4B'' + 8D''(J + \frac{1}{2})^2 \quad \dots\dots(3),$$

and evaluating the left-hand side for trial sequences in *J*, it was readily found that the values of *J* were near those given in table 1 and that *B''* had approximately the value 0.105, so that, from equation (2), *8D''* is approximately -2×10^{-7} . The ω in equation (2) was obtained from the vibrational analysis of Rochester and

Howell. The smallness of D' shows that the right-hand side of equation (3) must be very nearly constant, and we could limit the values of J as being either those given in table 1, or greater than them by unity. This difficulty, of course, arises from the fact that the values of J are all large, so that the quotient in equation (3) is never critical.

We could hope to derive help in this dilemma by calculating the upper-state constants B' and D' from the formula

$$\{R(J) - P(J)\} / (J + \frac{1}{2}) = 4B' + 8D' (J + \frac{1}{2})^2 \quad \dots\dots(4),$$

where D' is given by the analogue of equation (2) and ω is again obtained from the original work. However, we met with exactly the same difficulty, both sets of values of J giving nearly equally constant results. The difficulty was only removed

$B'(\text{cm}^{-1})$

0.08500

0.08400

0.08300

2 3 4 5 6 7 8 9 v'

Figure 1. Variation of B' with v' .

with the aid of the bands (2, 1), (3, 1) and (4, 1). The values of J for these bands could in turn not be decided absolutely, but we had the additional checks that the B_1'' derived from them must be smaller than B_0'' and that the values of B' , that is to say of B_2' , B_3' and B_4' , must be nearly linear with the values of B_6' , B_8' and B_9' derived earlier. That the latter condition is fulfilled by our ultimate choice is shown in figure 1.

Having determined uniquely the proper values of J for each branch of each band, we can proceed in the usual way to determine the constants B and D . The rotational term differences were extracted, those for the lower states being given in table 2. Using an approximate value for D_0'' in equation (3), we obtain a value of B_0'' for each difference, every difference being given equal weight so that a simple mean was taken. Using this nearly correct value of B_0'' we recalculate D_0'' from equation (2), using this improved value in equation (3), and recalculate B_0'' . We continue this process until constant values are obtained.

Table 2. Rotational term differences for the ground state

$$R(J-1) - P(J+1) = F''(J+1) - F''(J-1)$$

J	v''=0			v''=1		
	v'=6	v'=8	v'=9	v'=2	v'=3	v'=4
36				15.19		14.97
37				15.63		15.79
38	16.38					16.32
39	16.78				16.53	16.58
40	17.10			17.16	16.91	16.88
41	17.57			17.34	17.34	17.52
42	18.01			17.71	17.76	17.75
43	18.41			18.04	18.20	17.50
44	18.74			18.46	18.55	18.34
45	19.12				18.99	18.80
46	19.65			19.19	19.42	19.85
47	20.16			19.76	19.89	19.56
48	20.55				20.23	19.94
49	20.93			20.65	20.62	20.44
50	21.38			21.10	21.19	21.23
51	21.81		21.64	21.55	21.52	21.20
52	22.17		22.22	21.91	21.88	21.91
53	22.64		22.68	22.04	22.26	22.78
54	23.09	23.08	22.88	23.09	22.74	23.11
55	23.29	23.45	23.33	23.34	23.26	23.80
56	23.91	23.81	23.89	23.70	23.33	23.29
57	24.36	24.43	24.36	24.03	23.94	24.27
58	24.74	24.90	24.88	24.57	24.34	24.49
59	25.23	25.20	25.14	24.89	24.92	24.72
60	25.60	25.58	25.51	25.22	25.16	25.20
61	26.09	26.04	26.04	25.66	25.71	25.98
62	26.38	26.43	26.43	26.21	26.07	26.15
63	26.93	26.92	26.79	26.60	26.71	26.53
64	27.34	27.22	27.13	26.87	26.94	26.79
65	27.71	27.74	27.61	27.11	27.43	27.17
66	28.04	28.14	28.09	27.73	27.76	27.79
67	28.49	28.51	28.49	28.28	28.17	28.21
68	29.00	28.90	28.87	28.67	28.93	28.62
69	29.24	29.29	29.34	29.09	28.95	28.97
70	29.78	29.71	29.71	29.55	29.60	29.63
71	30.17	30.15	30.13	29.70	29.77	29.94
72	30.60	30.54	30.60	30.61	30.27	30.24
73	30.97	30.97	31.01	30.91	30.67	30.72
74	31.26	31.36	31.41	31.46	31.22	31.21
75	31.79	31.79	31.85	31.55	31.51	31.55
76	32.08	32.27	32.17	31.98	32.05	32.08
77	32.65	32.65	32.67	32.55	32.61	32.39
78	32.98	33.00	33.11	32.99	32.75	32.88
79	33.34	33.43	33.43	33.24	33.25	33.30
80	33.77	33.84	33.88	33.68	33.66	33.62
81	34.19	34.29	34.25	34.10	34.36	34.02
82	34.77	34.78	34.70	34.66	34.61	34.54
83	35.21	35.15	35.02	34.97	34.87	34.91
84	35.47	35.54	35.54		35.35	35.43
85	36.07	35.94	35.88		35.72	35.84
86	36.58	36.27	36.32		36.23	36.15
87	36.82	36.73	36.72		36.59	36.60
88	37.38	37.12	37.15		36.87	37.02
89	37.65	37.56			37.41	37.63
90	38.08	37.96	37.95		37.76	37.97
91	38.54	38.37	38.44		38.21	38.29
92	38.76	38.73			38.56	38.86
93	39.38	39.19			39.09	39.20
94	39.70	39.34			39.38	39.63
95	40.08	39.90			39.86	40.13
96	40.48				40.29	40.53
97	41.13				40.70	41.04
98	41.47				41.05	41.48
99	41.69				41.49	41.72
100	42.10				41.84	42.20
101	42.46				42.21	42.68
102	42.83				42.63	43.12

Note. The differences in the last column (v'=4) are obtained from unresolved doublets.

The results are given in table 3. The final mean value of B_0'' is obtained by weighting each band according to the number of measured lines in it. Similar procedure gives us B_1'' , etc. Assuming a linear relation amongst the B' values we have

$$B_v' = B_0' - \alpha (v + \frac{1}{2}) \quad \text{.....(5),}$$

and applying the rule of least squares we have

$$B_v' = 0.08560 - 29.55 \times 10^{-5} (v' + \frac{1}{2}) \quad \text{.....(6).}$$

Table 3

Band	(2, 1)	(3, 1)	(4, 1)	(6, 0)	(8, 0)	(9, 0)
B'' (cm. ⁻¹)	0.10477	0.10472	0.10510	0.10566	0.10557	0.10559
B' (cm. ⁻¹)	0.08485	0.08449	0.08427	0.08385	0.08305	0.08273

Mean values

B_0''	0.105614 cm. ⁻¹	r_0''	0.7552×10^{-8} cm.
B_1''	0.104741 cm. ⁻¹	r_1''	0.8406×10^{-8} cm.
B_v'	$0.08560 - 29.55 \times 10^{-5} (v' + \frac{1}{2})$	D_0''	-2.573×10^{-8} cm. ⁻¹
B_0'	0.10605 cm. ⁻¹	D_1''	-2.508×10^{-8} cm. ⁻¹

Note. The value of B_1'' derived from column (4, 1) is 0.10510, and the value of B_4' is 0.08427. Since the *P* and *R* branches are not separated in this band these constants have not been further employed although the value of B_4' is inserted in figure 1.

§4. DETERMINATION OF BAND ORIGINS

It is possible to obtain a value for ν_0 from every line by use of the formulae

$$\nu_0 = P(J) - B'J(J-1) + B''J(J+1) - D'J^2(J-1)^2 + D''J^2(J+1)^2 \quad \text{.....(7),}$$

$$\nu_0 = R(J) - B'(J+1)(J+2) + B''J(J+1) - D'(J+1)^2(J+2)^2 + D''J^2(J+1)^2 \quad \text{.....(8),}$$

with the values for B and D already found. The values of ν_0 so obtained were reasonably consistent and simple averages were taken. The results for each branch of each band are given in table 4. The row $\nu_h - \nu_0$ gives the calculated distances of the heads from the origins by means of the formula $(B' + B'')^2/4 (B'' - B')$ and we can thus give the calculated heads ν_h (calc.). The next row gives ν_h (obs.), the values for the heads actually observed by Rochester and Howell, whilst the final row gives the heads as calculated by them by the use of a least-square formula for all the heads of the A system. It will be noted that our analysis agrees more closely with these authors' calculations than with their separate observations.

Table 4. Band origins

	(6, 0)	(8, 0)	(9, 0)	(2, 1)	(3, 1)
ν_0, P	20318.17	20829.30	21084.88	18862.00	19120.90
ν_0, R	20318.67	20829.32	21083.44	18862.07	19119.80
ν_0 mean	20318.42	20829.31	21584.16	18862.04	19120.35
$\nu_h - \nu_0$	0.41	0.40	0.39	0.45	0.44
ν_h (calc.)	20318.83	20829.71	21084.55	18862.49	19120.79
ν_h (obs.)	20320.0	20832.3	21086.3	18863.0	19120.6
ν_h (calc.) R. & H.	20319.2	20830.4	21085.0	18862.2	19121.1

§5. ISOTOPE EFFECT

Lead has three main isotopes of masses 206, 207 and 208 having abundances 4, 3 and 7 respectively. Sulphur is relatively free from isotopes and has a mass of 32. Hitherto the isotopes of lead have only been identified in band spectra in the case of lead oxide⁽³⁾. Notwithstanding the relative abundance of the isotopes they were not obvious in the bands measured in the course of the present work, and it was only later that the weaker lines measured were so interpreted.

Taking ^{206}Pb as the isotope relative to the more abundant ^{208}Pb , we have for the ratio of the reduced masses

$$\rho^2 = (^{208}\text{PbS} \div ^{206}\text{PbS}) = 1.001295.$$

Table 5. Isotope effect, all lines not included in table 1

(6, o)			(6, o)			(6, o)		
	δ	δ (calc.)		δ	δ (calc.)		δ	δ (calc.)
P 38	0.40	0.45	R 78	0.70	0.80	P 82	0.61	0.75
P 39	0.42	0.45	P 71	0.77	0.80	R 90	0.63	0.74
P 40	0.67	0.45	R 79	0.84	0.80	P 83	0.73	0.74
P 46	0.78	0.90	P 72	0.77	0.79	P 84	0.72	0.74
P 47	0.83	0.89	R 80	0.76	0.79		1.57	—
P 48	0.88	0.88	P 73	0.75	0.79	R 92	0.51	0.73
P 51	0.99	0.87	R 83	0.76	0.78	P 85	0.66	0.73
P 52	0.85	0.87	P 76	0.70	0.78	P 87	0.76	0.72
P 53	0.75	0.87		1.46	—	P 88	0.82	0.72
P 55	0.81	0.86	R 84	0.75	0.77		0.67	0.71
P 61	0.83	0.84	P 77	0.67	0.77	P 89	1.48	—
P 62	0.92	0.83	R 85	0.61	0.77	R 97	0.55	0.71
P 63	0.74	0.83	P 78	0.80	0.77	P 90	0.55	0.71
P 67	0.82	0.81	R 86	0.75	0.76	P 91	0.54	0.70
R 76	0.70	0.81	P 79	0.67	0.76	R 99	0.58	0.70
P 69	0.80	0.81	R 88	0.72	0.75	R 100	0.62	0.69
P 70	0.69	0.80	P 81	0.74	0.75	R 101	0.61	0.69
				1.41	—	P 94	0.60	0.68
			R 89	0.77	0.75	R 104	0.82	0.67

(8, o)			(8, o)			(8, o)		
	δ	δ (calc.)		δ	δ (calc.)		δ	δ (calc.)
R 54	0.49	0.60	P 65	1.02	1.14	P 81	0.51	0.54
P 52	0.56	0.60	R 74	1.10	1.14	R 89	1.09	1.07
R 60	0.56	0.59		0.59	0.57	P 83	0.54	0.53
R 61	1.12	1.19	R 75	1.01	1.13	P 84	0.50	0.53
R 61	0.98	1.18	R 76	0.62	0.56	R 92	1.05	1.05
R 62	0.50	0.59	R 77	1.04	1.12	P 85	0.52	0.53
	1.15	1.18	R 78	1.03	1.12	P 86	0.50	0.52
P 56	0.53	0.59	R 79	1.15	1.12	R 95	0.97	1.04
R 65	1.06	1.17	R 80	1.08	1.11	R 97	0.94	1.03
R 67	1.03	1.17	R 81	1.01	1.11	R 98	0.47	0.51
R 69	1.15	1.16	R 82	1.04	1.10		1.63	—
P 62	0.55	0.58	P 76	0.54	0.55	R 100	2.44	—
R 70	1.08	1.15	P 78	0.60	0.54	R 101	0.93	1.00
R 71	1.05	1.15		0.57	0.54	P 94	0.46	0.50
P 64	0.45	0.57	R 86	1.05	1.08	R 102	0.57	0.50
R 72	1.16	1.15	R 87	1.08	1.08	R 103	1.76	—

Table 5 (cont.)

(9, 0)			(9, 0)			(9, 0)		
	δ	δ (calc.)		δ	δ (calc.)		δ	δ (calc.)
R 51	0.71	0.70		0.71	0.66		0.55	0.62
R 52	0.67	0.70	R 73	1.57	1.33	R 90	2.99	—
	1.30	1.39		1.94	—		3.79	—
R 53	0.97	0.70	R 74	0.61	0.66	R 91	0.57	0.62
R 55	0.55	0.69		0.64	0.66		1.39	1.23
R 56	0.65	0.69	R 75	1.34	1.31	R 92	0.93	—
R 57	0.68	0.69		2.15	—		2.27	—
R 58	0.67	0.69	R 76	0.63	0.65		0.60	0.61
R 59	0.59	0.68		1.21	1.30	R 93	1.27	1.22
	1.25	1.37	R 77	0.56	0.65		2.41	—
R 60	0.62	0.68	R 78	0.62	0.65		0.62	0.61
R 61	0.70	0.68	R 79	0.64	0.65	R 94	1.19	1.22
	1.34	1.36	R 80	0.53	0.64		2.10	—
R 62	0.75	0.68		1.69	—	R 95	0.47	0.61
R 63	0.69	0.68	R 81	0.61	0.64		2.35	—
	1.30	1.36	R 82	0.60	0.64		2.78	—
R 64	0.65	0.68	R 83	0.58	0.64		0.58	0.60
	1.28	1.35	R 84	0.70	0.63	R 96	1.08	1.21
R 65	0.55	0.67		2.70	—		1.36	—
	1.25	1.35	R 85	0.64	0.63		3.00	—
R 66	0.54	0.67		1.43	1.26	R 97	1.28	1.20
	1.30	1.35	R 86	0.67	0.63		1.63	—
R 67	0.67	0.67		1.17	1.26		3.05	—
R 68	0.82	0.67	R 87	0.60	0.63		0.61	0.60
R 69	0.55	0.67		1.28	1.25	R 98	1.40	1.20
	1.11	1.35	R 88	2.44	—		1.90	—
R 70	0.65	0.66		0.50	0.62		2.40	—
	0.61	0.66	R 89	0.62	0.62		1.04	1.19
R 71	1.27	1.33		1.09	1.24	R 99	1.64	—
	1.84	—		1.59	—		2.21	—
R 72	0.71	0.66					2.79	—

As is well known, the isotopic shift can be regarded as the sum of two effects; (i) a bodily displacement of the whole band and (ii) a displacement of each line by an amount approximately proportional to its wave-number distance from the band origin. The first effect is given by

$$(\rho - 1) \left[(v' + \frac{1}{2}) \omega_v' - (v'' + \frac{1}{2}) \omega_v'' \right] \quad \dots\dots(9),$$

and substituting for the ω 's and writing

$$v'' = 0, v' = 6, 8 \text{ and } 9$$

we have for the bands (6, 0), (8, 0) and (9, 0) respectively shifts amounting to 0.960, 1.308 and 1.476 cm^{-1} , all positive. The second effect is negative and is given by

$$(1 - \rho^2) (\nu_0 - \nu) \quad \dots\dots(10),$$

where ν_0 is the band-origin and ν is the wave-number of the line in question. The result is that each line in the main *P* and *R* branches, if due to ^{208}Pb , should have a line due to the isotope ^{206}Pb on its more refrangible side, as above calculated, together with a line due to ^{207}Pb midway between them and of a little lower intensity than that due to ^{206}Pb .

In table 5 are given all the lines measured on the plates which remained after the main series given in table 1 for (6, 0), (8, 0) and (9, 0) had been withdrawn.

The first column in the table gives the nearest *P* or *R* line on the red side of each of these extra lines; the corresponding wave-numbers have already been given in table 1. The second column, under δ , gives the amounts by which these new lines exceed in wave-number the corresponding lines in the first column, whilst the third column, δ (calc.), gives the corresponding displacements as calculated by the above formula with either ^{206}Pb or ^{207}Pb or both, as may be appropriate. It will be seen that the great majority of the remaining lines are thus satisfactorily accounted for. The extra lines in the tail of (9, 0) are probably due to the moderately strong band (10, 1) which occurs here. The fact that only a fraction of the isotope lines have been observed is probably due to a number of factors; for instance, the temperature of our absorption tube was kept down to an extent which was sufficient to show clearly the main structure of the bands with the minimum complication from overlapping bands. Thus the isotope lines recorded were quite faint and were just distinguishable from a very complex, though weak, background.

For the bands (2, 1), (3, 1) and (4, 1) the above formulae give results which are too small for us to be able to detect and throughout we have blends of all three lines.

The vibrational effect given by equation (9) is much greater for large values of v'' and small v' . In the (0, 7) band-head at $15,837\text{ cm}^{-1}$ there is the further effect that over a considerable range the *P* and *R* branches are superposed so as to produce a simple spectrum and strong lines. The use of Rochester and Howell's values $\omega' = 261.1$ and $\omega'' = 428.14$ with equation (9) gives

$$\Delta\nu = -1.996\text{ cm}^{-1}$$

The rotational effect given by equation (10) also is easily calculable. On examining a plate in the first order the isotopes were quite distinct and table 6

Table 6. Superimposed *P* and *R* lines in the band (0, 7) and their corresponding isotopes

$\nu\text{ (cm}^{-1}\text{)}$	$-\Delta_1\nu\text{ (cm}^{-1}\text{)}$	$-\Delta_2\nu\text{ (cm}^{-1}\text{)}$
15,694.69	1.00	2.05
91.63	1.18	2.07
88.48	1.01	2.21
85.14	—	2.26
81.95	1.15	2.32
78.65	1.08	2.28
75.34	—	2.04
72.01	1.04	2.14
68.53	1.13	2.07
65.18	1.11	2.09
61.58	0.96	2.05
58.08	1.06	2.14
54.54	—	2.26
51.02	—	—
47.46	—	—
43.82	1.10	2.09
Mean	1.08	2.15

$\Delta_2\nu$ applies to ^{206}Pb . $\Delta_1\nu$ applies to ^{207}Pb .

gives some measurements made. The rotational effect varies over the observed range uniformly from -0.18 to -0.25 cm^{-1} . The sum of the two effects as observed is entered for the two isotopes after each line. The mean effect for ^{206}Pb is seen to be double that for ^{207}Pb . The calculated mean value for ^{206}Pb is given by -1.996 cm^{-1} for the vibrational effect and -0.21 cm^{-1} for the rotational effect. The sum, -2.21 cm^{-1} , is in excellent agreement with the observed -2.15 cm^{-1} , since the formulae (9) and (10) are approximate and a small variation in the ω s would bring them into agreement.

Finally, the excellence of the various isotope results verifies the carrier as lead sulphide and confirms the vibrational analysis made by Rochester and Howell.

§ 6. ACKNOWLEDGEMENTS

We are indebted to Prof. W. L. Bragg, F.R.S., for the facilities placed at our disposal, to Prof. W. E. Curtis, F.R.S., for valuable criticism, and to Dr G. D. Rochester and Dr H. G. Howell for supplying us with much information not contained in their original articles.

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DEMONSTRATIONS

A LABORATORY METHOD FOR THE DETERMINATION OF THE PERIOD OF THE TRANSVERSE OSCILLATIONS OF FLEXIBLE RODS BY MEANS OF A PHOTOELECTRIC CELL. By G. A. BENNETT and J. E. CALTHROP, Queen Mary College

Demonstrated 28 January 1938

A UNIFORM bar of length l and of linear density m is rigidly clamped at one end and has a mass M suspended at the other. If I is the moment of inertia of the section about the trace of the neutral section, and E is Young's modulus for the material, the period T of transverse oscillations is given by

$$T = 2\pi \sqrt{\frac{(M + 0.24ml) l^3}{3EI}}$$

or

$$T^2 = \frac{4\pi^2 M}{3EI} + \frac{0.32\pi^2 ml^4}{EI}.$$

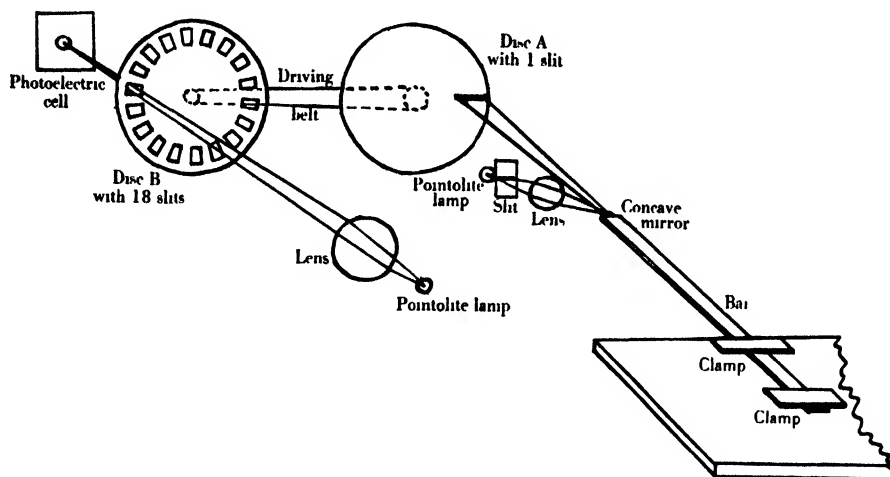


Figure 1

To verify this relation two experiments may be performed. (1) M is made equal to zero, l is varied, and T^2 is plotted against l^4 . (2) l is made constant, M is varied, and T^2 is plotted against M . The slopes of the expected straight lines should give a value of E .

In the method adopted for measuring T a slit is illuminated by light from a pointolite-lamp as shown in figure 1. By means of a lens the light is focused on a small concave mirror attached to the end of the vibrating rod, so as to give a sharp image on a distant ground-glass screen. In front of the screen is placed a rotating cardboard disc A provided with a single slit so that a steady central image is seen on the screen only when the period of the disc is equal to the period of the bar

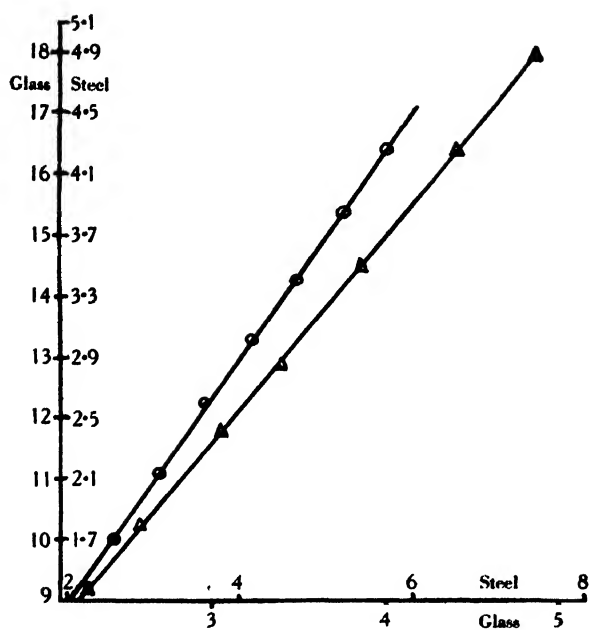


Figure 2

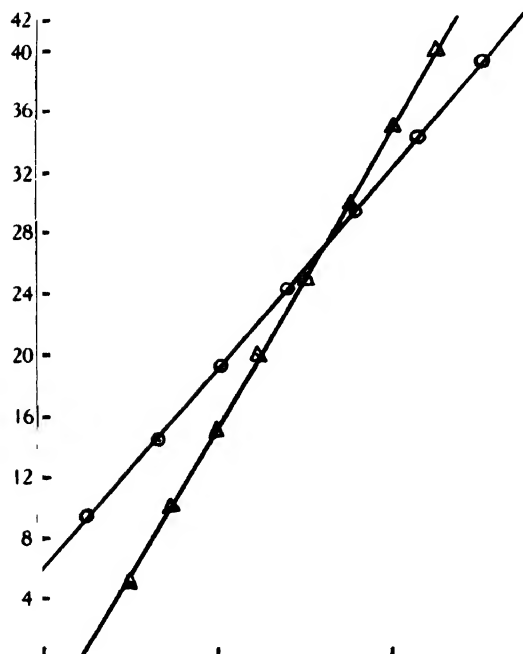


Figure 3

or some simple fraction of it. The rotating disc is geared to the axle of an electric motor, which is provided with another disc *B* having eighteen slits. Light from a pointolite lamp passes through these slits so that a photoelectric cell is illuminated intermittently. The cell is joined to a 2-stage or 3-stage valve amplifier, so as to produce in telephone receivers or a loudspeaker an audible note, the frequency of which is determined by obtaining beats with a sonometer wire. The gearing-ratio is found by replacing the disc having a single slit by one having thirty-six slits and illuminated so as to give an audible note in the photoelectric circuit. Thus if n is the frequency of the motor and x the gearing-ratio, the first disc gives a note of frequency $18n$ and the second a note of frequency $36n/x$. From the ratio of the corresponding lengths of the sonometer wire x is found. Figure 1 represents the arrangement of the apparatus. The diagram of the photoelectric circuit is omitted. Figure 2 shows a plot of l^4 and T^2 for steel and glass, and figure 3 a plot of M and T^2 for the same materials. The corresponding values of Young's modulus are as shown in the table.

Table. Young's modulus

Material	l^4 and T^2	M and T^2 (10^{12} dyne/cm ²)
Steel	2.09	2.07 ₆
Glass	7.28	72.5

The frequencies of the rods were of the order 10 to 20 c./sec.

SOME EFFECTS PRODUCED BY THE IRRADIATION OF LIQUIDS AND GELS WITH ALPHA, BETA AND GAMMA RAYS AND NEUTRONS.* By F. L. HOPWOOD and J. T. PHILLIPS

Demonstrated 11 March 1938

DURING an investigation of some of the effects of neutrons on substances of biological importance⁽¹⁾ it was found desirable to reinvestigate some of the effects due to alpha, beta and gamma rays which had been observed by ourselves and others in some cases before the neutron was discovered. The necessity for doing this arose in part from the fact that the only neutron-sources available for experiment emitted beta and gamma rays also. In the course of this work some phenomena were observed which appeared to be of sufficient general interest to bring before this society.

Decomposition of dilute solutions of hydrogen peroxide by gamma rays and neutrons. Figure 1 shows the action of gamma rays and neutrons on a dilute solution of hydrogen peroxide. The progress of the reaction was followed by means of standard chemical titrations.

The upper line (*A*) shows the combined effect of the neutrons and gamma rays from a mixture of beryllium and radium salt in breaking down the solution.

* A more complete description of some of these experiments together with a discussion of their quantitative aspects will be published shortly.

Line *B* shows the effect obtained from a strictly parallel control experiment using gamma rays only. Line *A-B* gives the effect due to neutrons as the difference of *A* and *B*.

All the graphs show a linear relation between the chemical decomposition and the amount of radiation absorbed and thus afford a basis for a chemical method of measuring the strength of a neutron source.

Liquefaction and regelation following irradiation of a gel. A small thin-walled glass capillary tube containing radium emanation (radon) is laid on the surface of a block of gel containing 6 per cent gelatine in water. The combined action of the beta and gamma rays causes the gel to liquefy locally, thus permitting the descent

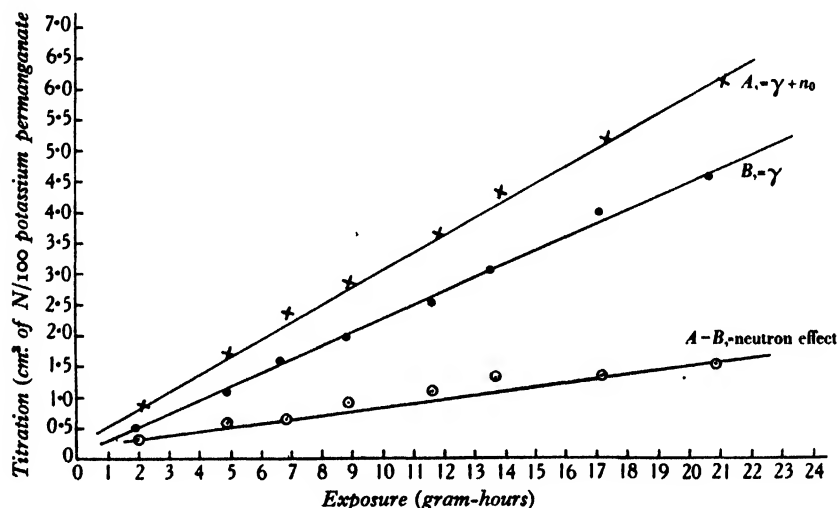


Figure 1. Neutron and gamma-ray irradiation of hydrogen peroxide. Concentration of solution, 0.63 g./l.; volume used for irradiation, 100 cm³; sources, *A*, 290 mg. of radium as chloride + 4.4 g. of beryllium; *B*, 290 mg. of radium as sulphate.

of the capillary tube. Following the descent, continued irradiation and interdiffusion between the liquid and unmodified gel results in regelation. Ultimately when the radon is "dead" the capillary tube is completely embedded in the gel (figure 2).

A similar tube filled with air remains on the surface of the gel.

Effect of gamma rays and neutrons on the formation of Liesegang rings. It was discovered by R. Liesegang⁽²⁾ that periodic precipitation of silver chromate will take place when a drop of silver nitrate solution is placed upon the surface of a glass plate covered with a shallow layer of gelatine impregnated with potassium bichromate. The precipitate takes the form of a disc surrounded by concentric coloured rings of varying thickness and diameter.

Contrary to the experience of others⁽³⁾, we have found that sufficiently intense irradiation of the gel during the formation of the rings causes marked changes in their structure. This can be seen in figures 3, 4 and 5. In some cases the effect is enhanced by the addition of a dye to the gel.

Developability of silver grains in a photographic emulsion when bombarded by alpha particles. It is well known that the energies of protons and alpha particles can be investigated by studying their ranges in photographic emulsions as indicated by the tracks of developable silver grains which they produce⁽⁴⁾.

Using this method, we have observed an anomalous effect when streaks of a solution of RaC, drawn by a rubber pen on a photographic plate, have been used as sources of alpha particles. In many cases two wide bands of tracks have been observed at one edge of a streak which are separated by a region practically devoid of them (figure 6). The absence of tracks in this region shows that, owing probably to some lack of neutrality in the solution, the silver grains cannot be made developable by alpha-ray bombardment, although alpha particles can be shown to be present in abundance. Evidence for this is afforded by the defect in formation of asters when many tracks originate at one spot. Figures 7 and 8 show a normal aster and an abnormal aster respectively.

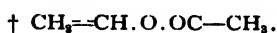
Turbidity of irradiated protein solutions. As is shown by the increased turbidity of solutions after irradiation, many proteins are denatured by irradiation with alpha, beta or gamma rays. The addition of sodium chloride to a solution of egg albumen is said to enhance this effect⁽⁵⁾.

Figure 9 shows that the opposite effect can also occur.

Polymerization of unsaturated hydro-carbon compounds. It is well known that a number of chemical compounds can be polymerized by the action of ultra violet light, and the same effect is sometimes produced by alpha rays from radioactive substances^(6, 7).

We have found that styrene* and vinyl acetate† can be polymerized at room temperature by alpha rays, beta rays and gamma rays either acting in conjunction with neutrons or alone.

The polymerization is demonstrated by the increase in viscosity of the liquids, streaming polarization, and solidification.



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Rutherford at McIdourne, 1925

OBITUARY NOTICES

ERNEST, FIRST BARON RUTHERFORD OF NELSON, NEW ZEALAND, AND CAMBRIDGE

AUGUST 30, 1871—OCTOBER 19, 1937

M.A. New Zealand, 1893; B.Sc. and 1851 Science Scholarship, 1894; B.A. Research Degree and Coutts-Trotter Studentship, 1897; D.Sc. New Zealand, 1901; LL.D. Pennsylvania, Wisconsin, McGill, Birmingham, Edinburgh, Copenhagen, Glasgow; Ph.D. Giessen, Yale; D.Sc. Cambridge, Dublin, Durham, Paris, Oxford, Liverpool, Melbourne, Toronto, Bristol, Cape Town, London, Leeds; D.Phys. Clark; F.R.S., 1903. Macdonald Professor of Physics, McGill University, Montreal, 1898–1907; Langworthy Professor, University of Manchester, 1907–19; Cavendish Professor, University of Cambridge, 1919–37. Rumford Medal, 1905; Copley Medal, 1922; Barnard Medal, 1910; Franklin Medal, 1924; Albert Medal, 1928; Faraday Medal, 1930; Bressa Prize, 1908; Nobel Prize, 1908; Order of Merit, 1925; President of the Royal Society, 1925–30; President of the British Association, 1923; Guthrie Lecturer, 1927; President of the Institute of Physics, 1931–3; Knight, 1914; First Baron, created 1931.

§ 1. EARLY YEARS IN NEW ZEALAND

Compiled by Prof. C. C. FARR, F.R.S., Canterbury College, Christchurch, New Zealand*

Lord Rutherford as a schoolboy. The following notes were drawn up by one of his sisters, Mrs Sergel, in consultation with another sister, Mrs Bell, and his mother, Mrs James Rutherford:

“He was one of twelve children, being the fourth child and second son of James and Martha Rutherford. He was always of a happy and loving disposition, besides being very unassuming in all his ways. In his holidays he was always willing to turn his hand to any little tasks, from painting the house to managing the ropewalk connected with the flax mill of his father. Also his fondness for music was very pronounced, his constant urging other members of the family to play and sing being in his opinion a pleasant accompaniment to his studies. One time he had a fad for taking photographs of his family, brothers and sisters, with a home-made camera, and he was continually taking clocks to pieces, evidently anxious to find out first hand the actual processes by which such a wonderful mechanism functioned. One of his chief physical interests was single-stick, which in his youth was a prominent exercise or physical-training method in secondary schools of his time. He found his skill particularly useful when he was made librarian at Nelson College, as he kept order with a wicket, and possibly his prowess as a swordsman instilled the necessary respect for authority. He was very fond also of making model water wheels, probably owing to the fact that nearly all the flax mills

* Part of the matter in this section has already been published in *The Times*. It is reproduced here by kind permission of *The Times* and of Prof. Farr.

which his father owned were working by means of water power. Mr Rutherford, senior, was particularly skilful in installing water mills, and the interest of the young student was naturally attracted to this form of mechanical movement. After passing one of his earlier examinations he was offered some position, which, however, he fortunately did not accept, deciding to continue his studies, although there is a suggestion that times were not very good for his parents, and the temptation to go early to earn money was therefore pronounced. However, wiser counsels prevailed.

"The reading of books was always a fondness of his. Anything at all seemed to interest him, even the very lightest of literature, something easy to follow, evidently forming a recreation to his mind. He was, however, specially fond of Dickens when young, and would welcome any opportunity to read out loud to younger members of the family, joining most heartily with his huge laughter, as it seemed to them, the various humorous incidents of *Pickwick Papers*. In holiday time he was often asked to teach his younger sisters, who in the ordinary way were instructed by a governess. In order to hold their attention or keep them quiet, he used to tie their pig-tails together. And when asked by his mother to teach the girls something he would generally reply, 'If they are mustered by nine o'clock, I will, but you must do the mustering.'

"Saturdays were often employed birds'-nesting, spearing eels in the river, catching brook trout in the pools in the bush, and long walks towards 88 Valley. And once when Rutherford was living at Havelock a hop-picking holiday was arranged. Mrs Rutherford, his mother, went to keep house at an old residence at Foxhill, for the four boys, Ernest, Jim, Herbert and Charlie. They earned about £13 in six weeks, picking hops. Ernest had a narrow escape while bathing during dinner hour in the Wai-iti river. He and one of his brothers were bathing and neither could swim. Ernest got out of his depth. Fortunately Jim just managed to reach him and get him out. It was kept a dead secret as otherwise bathing would have been stopped. Both boys were badly frightened. When the family moved to Taranaki, Ernest tried his hand at pheasants and wild pigeons. He used to get a horse and ride through the bush, often through deep mud, to reach the objective just as the sun was rising. There were three miro trees, the berries of which attracted the pigeons. They came in large numbers, but the ammunition was home made and the guns poor, so that he could not bring any down out of the high trees. The birds sitting on the high trees formed a very small target, until Ernest suggested a solution, and that was to fire when the birds were about to alight, which they would do with their wings outspread. On one occasion sixteen were bagged."

At Nelson College. The following notes were contributed by Mr C. H. Broad who was a schoolfellow of Rutherford at Nelson College, of which he afterwards became headmaster:

"Ernest Rutherford entered Nelson College as the holder of an Education Board Scholarship in 1887. He remained a pupil here for three years, gaining a University Junior Scholarship in 1889. He and I were in the fifth and sixth forms

together during the whole of his stay at Nelson College. I can well remember his arrival at the College. He had been placed by the headmaster, Mr W. J. Ford, in form V, an unusually high form for a new scholarship holder, and we, i.e. the gods of the fifth form, wondered who this fair-haired interloper was. We soon found out! During his three years' stay at the College he entered into the full life of the school in every way, games as well as study, and although he could never be described as an athlete he was nevertheless a forward in the first fifteen in his last year. What always particularly struck me about him was his extraordinary powers of concentration, even in the midst of the greatest turmoil. In the sixth form (not in school time of course) there was at times considerable uproar—books flying, etc.—and yet Rutherford would be absolutely oblivious to the confusion, his mind following up some mathematical point, geometrical rider, or the like. I am afraid some of us used to take full advantage of his abstraction in various boyish ways, banging him on the head with a book, etc., and then bolting for our lives. Another thing I well remember about Rutherford was his habit of strolling about with Dr W. S. Littlejohn on the half-holiday, up and down little-frequented streets near the College, Littlejohn drawing diagrams in the dust of Hampden Street and he and Rutherford discussing them. You could get a good deal of information from Dr Littlejohn, now Headmaster at Scots College, Melbourne, but at that time mathematical and science master at the College, to whom Rutherford owed so much of his early grounding in these subjects. It is interesting to note that in addition to mathematical prizes Rutherford also gained the Stafford scholarship for English history, the Simmons prizes for English literature, the senior classical prize and also the French scholarship, so that he was a boy of many parts. As far as I can ascertain, his academic successes while at school here were as follows: 1887, reading prize, Stafford scholarship for history; 1888, senior English literature scholarship, French scholarship, classical prize, form VI, and mathematics prize, form VI; 1889, Simmons prize for English literature, Latin prize, form VI, mathematics prize, form VI. As regards science, it has to be remembered that in those degenerate days chemistry was optional with French, and consequently Rutherford began his science late in his career here and then he was practically taken alone in physics and chemistry by Dr Littlejohn. Science has come into its own now, but in those days it was sadly neglected. Littlejohn, however, raised it to a very high standard in Nelson, but Rutherford was in the early stages of the process."

At Canterbury College. The following notes were drawn up by Mr R. M. Laing, M.A., a fellow undergraduate at Canterbury College at the time of Lord Rutherford's student days, with the help of Mr S. Page, B.Sc., who was Demonstrator in Chemistry and Physics to Prof. Bickerton during the same period:

"Rutherford came to Canterbury College in 1890 with a Junior University Scholarship. It was then a very small institution with some seven professors and 150 regular students. A laboratory for physics and chemistry was housed in a galvanized iron building, not much more than 60 feet long, under the control of Professor A. W. Bickerton. Mathematics was taught by Professor C. H. H. Cook.

To these two professors Rutherford naturally gravitated. They were of very opposite types. Professor Bickerton was heterodox in all his views, and very erratic in his methods of teaching, but at the same time highly original. He never gave out the formal thoughts of another, but expressed everything in his own terms and from his own point of view. He had no knowledge of mathematics, but worked out his mechanical and physical problems by graphic methods, when graphics were scorned by the more orthodox professor of mathematics, and before they had obtained the position they now have in physical science. He had wide and far-reaching views on the evolution of the universe, and though these views have not in the main been confirmed by subsequent research, yet amongst them were some novel ideas which have since been established by astronomical physicists. Though Professor Bickerton's teaching may have been of little value for the dull student in many ways it suited Rutherford's type of mind. Bickerton was an enthusiast for research and had the power of making others share his enthusiasm. When most men thought that physics had reached an *impasse* beyond which it could go no further, he believed that it was only at the beginning of world-shaking discoveries, and though his reasoning may have been crude, yet his conclusion was correct and has since been amply justified. Naturally such a professor filled Rutherford with love for his work, and taught him to break away from the trammels of the hide-bound physical science of the day. For students of some individuality Professor Bickerton was an excellent stimulant, even though he did not by any means keep himself abreast of the developments of his own day and time. On the other hand, the mathematical professor, C. H. H. Cook, thoroughly orthodox in all his views and strictly scholastic in his methods, and within his limitations a very able man, applied the brake to the young student and prevented his speculations from leaving the ground of fact. Here Rutherford obtained a sound instruction in the mathematics of the day, with which he was able to control the wilder flights of his physical teacher.

"Rutherford came to Canterbury College a boyish, frank, simple and very likeable youth, but with no precocious genius. Two others of his contemporaries at least were regarded by his teachers as equal to himself in ability and brilliance, but these have not distinguished themselves as he has done. The secret of Rutherford's success has been that once he saw the goal he turned neither to the right hand nor to the left, no matter how fascinating the byways might appear, but went straight on to the central problem of his research, the structure of the atom. No doubt in his earlier papers he was groping for a pathway, but as we shall see it was soon found and has never been left; and his whole progress has been one long story of increasing success. He appears as No. 338 in the register of students of Canterbury College, and his career there is thus described (*History of Canterbury College*, 1927, p. 203): '1890, Exhibition in mathematics; 1891, exhibition in mathematics; 1892, exhibition in experimental science and mathematics; 1893, B.A., senior scholarship in mathematics; 1894, 1st class honours, mathematics, and 1st class, physical science; 1894, 1895, Exhibition science scholarship in electricity; 1901, D.Sc. (N.Z.).' Now the 1851 *Exhibition Scholarship* was awarded once in about

three years to the New Zealand student showing most promise in some branch of science, and enabled him to go to an English university and carry on his studies there.

"For his thesis in physics, Rutherford had carried out an inquiry into the magnetization of iron by high-frequency discharges. This research was done in a miserable, cold, draughty, concrete-floored cellar, which was usually known to the students as the 'Den', and in which they were accustomed to hang up their trenchers and gowns. There was no other accommodation available. This Den will surely be historic in future. Rutherford's investigation—his first paper—is published in the *Transactions of the New Zealand Institute*.^{*} The first paragraph of the paper is as follows: The subject of the magnetization of iron in very rapidly varying fields has been touched upon more or less fully by different scientists, notably Dr Lodge, Professor J. S. Thomson, Hertz, and a few others. In Dr Lodge's *Modern Views of Electricity* we find the following: 'But in the case of a discharge of a Leyden-jar iron is of no advantage. The current oscillates so quickly that any iron introduced into the circuit, however subdivided into thin wires it may be, is protected from magnetism by inverse currents induced in its outer skin, and accordingly does not get magnetized, and, so far from increasing the inductance of the discharge circuit, it positively diminishes it by the reaction effect of these inducted currents; it acts, in fact, much as a mass of copper might be expected to do.' Rutherford was able to show, in opposition to the prevailing scientific opinion of the day, that iron is strongly magnetic in rapidly varying fields, even when the frequency is over 100,000,000 per second. It is obvious that in those days to carry out such an investigation required high powers of experimentation in order to deal with frequencies of such an order. In fitting up his apparatus Rutherford received considerable assistance from Mr S. Page, the demonstrator in the laboratory. This is not the place to discuss the details of the experiment; but suffice it to say that for magnetization purposes needles were used which ranged in diameter from 0.1 in. to less than 0.01 in. For lower rates of oscillation ordinary piano wire was used; but when the rates of oscillation were of the order of 10^{-8} per second a more delicate detector was required. This induced Rutherford to consider the dumb-bell oscillator of Hertz. The use of this detector led naturally to the study of the Hertzian waves, as they were then termed. Rutherford's second paper published in the following year[†] was entitled 'Magnetic viscosity'. In order to investigate small intervals of time, Rutherford invented a time apparatus which was capable of measuring intervals up to 0.00001 sec., a remarkable degree of precision considering the crude apparatus with which he had to work. The time was measured by the space through which a body making and breaking contact fell, and careful and minute corrections were made to ensure accuracy. By this time Rutherford was able to send Hertzian waves from one end of the old 'tin shed', as it was called, to the other, and pick them up by means of a detector of his own invention. Thus he was started on a career for the investigation of radiations that led him to an explanation of the radio-activity of radium, when other investigators were baffled by the phenomena there presented.

^{*} *Trans. N.Z. Inst.* 27, 481 (1895).

[†] *Trans. N.Z. Inst.* 28, 182 (1896).

"But Rutherford's whole time was naturally not taken up by his researches. He was a normal healthy student amongst other students. In the outdoor world he held his own at least. The chief field sport of those days, as it is still at Christchurch, was rugby football. Rutherford played in the first fifteen of Canterbury College as a forward, though without any particular distinction. On the whole he was of a conservative type of mind, though very fond of discussion. With fellow students he would sometimes discuss till the small hours of the morning the writings and personalities of such authors as Tennyson and George Sand, who were much in vogue then. Further opportunities for discussion came with the establishment of a Science Society among the students. Some of the more radical of the students thought that scientific topics were not given a fair and full hearing in the community and that it would be an excellent thing for education in the University if some group could be formed to discuss what in those days were considered advanced forms of thought. With this end in view a Science Society was formed in 1891. Rutherford was one of the original members, and amongst its founders was the late Mr W. G. Pye, a man of broad philosophic thought and full of ideas then considered heterodox. One of his heresies was that the atoms could not be discrete particles, but that there must be some more fundamental form of matter, more primitive even than the atom. Consequently the first subject for discussion was the evolution of the elements. Thus early was Rutherford led to consider the possibility of subatomic structure. Other subjects considered were, evolution in biology, evolution in psychology, evolution in morality and religion. Now in Christchurch at that time it was considered scarcely respectable to believe in evolution, and the University community was rather shocked at the open discussion of such subjects by young students. Rutherford himself felt that we had gone rather too far, and was with difficulty persuaded to take the secretaryship of the Society in 1893. In 1894 he read a paper on the then new subject of electrical waves and oscillations. The following is the note in the minute book of the Society on the address: 'Mr Rutherford then read his paper on electrical waves and oscillations, in which he dealt with oscillatory discharges in general, referring more particularly to the recent researches of Hertz and Tesla and their bearing on Maxwell's theory. The paper was very fully illustrated by experiments performed by Mr Rutherford with the assistance of Mr Page and Mr Erskine, the most striking of the experiments being a reproduction on a small scale of Tesla's experiments on the rapidly alternating currents.' Thus early had Rutherford embarked upon the course of Wordsworth's Happy Warrior,

the generous Spirit, who, when brought
Among the tasks of real life, hath wrought
Upon the plan that pleased his boyish thought;
Whose high endeavours are an inward light
That makes the path before him always bright,
Who, with a natural instinct to discern
What knowledge can perform, is diligent to learn.

a course from which he did not depart throughout his career."

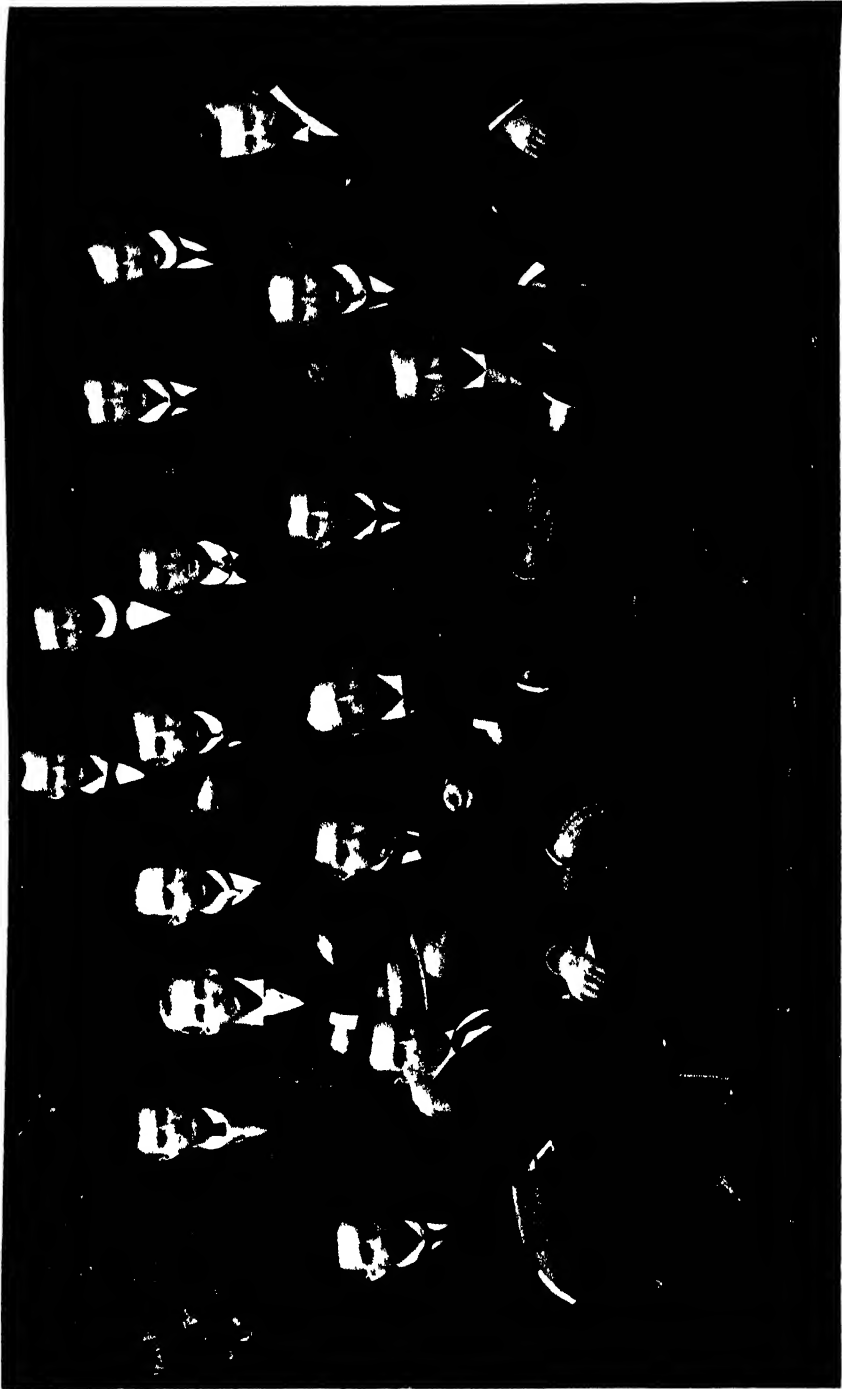
On the staff of the Boys' High School, Christchurch. The following notes are by Mr O. Gillespie, who was a pupil when Lord Rutherford was a master at the Boys' High School, Christchurch. The Mr Walton mentioned is another old master, now dead:

"Lord Rutherford is with me a dim but very delightful memory. He endeavoured to teach mathematics to a form of boys to which I belonged. He certainly made no impression on me and I am doubtful whether his unique methods were any use to the ordinary monkey-minded schoolboy. He was, of course, entirely hopeless as a schoolmaster. Disorder prevailed in his classes, not quite so overt as the Auckland riots but far more continuous. I do not remember myself following any one of his intellectual processes on the blackboard, the medium through which he endeavoured to illustrate them. They were done like lightning. When he detected some more than usually noisy boy he sent him sternly for the Appearing Book. All the lad had to do to escape the consequences of his misdeeds was to stay out of the class room long enough for Rutherford's enormous mind to have bulged in some other direction, and sneak back to his seat, when he would inevitably not be noticed. Rutherford had the quite modern theory too of giving the boys the Answer Books, observing that the working was what really mattered. I am afraid, though, that he did not really too carefully inspect the working as I got quite good marks personally by filling in the answer correctly and working back a mere mass of xs , ys etc., which were put in more for their decorative effect than anything I understood about. The main characteristic of the mob mind of a schoolboy class is its ape-like cunning, and we certainly had him added up as a genial person whose interests had nothing to do with the keeping in order of small boys. He used to blurt suddenly into anger which was succeeded by a sort of desperate calm. This latter mood was hailed with real joy by all pupils. I remember one pupil very well, though I cannot remember his name, who was dealing with the problem of proportion. The questions and answers were something like these (mind you this is only a shadowy memory) but I remember that even my very defective mathematical fatuity saw something comic in the argument. The sum was something like this: If 9 horses plow 28 acres in 16 weeks how long will it take 5 horses to plow 11 acres. The pupil being cross examined divided by the number of horses and Rutherford explained that five horses would take longer than nine and that, therefore, the days required should be multiplied. The pupil simply said, 'Mr Walton said we had to divide and I am going to divide.' Rutherford simply dropped his pencil and looked hopeless. I am afraid as a schoolmaster he would have been a very bad misfit as First Assistant at Fernside or Cust. This, of course, is to his eternal credit. My recollection is that we all liked him personally immensely."

§ 2. RUTHERFORD WHEN A RESEARCH STUDENT AT CAMBRIDGE

By Sir J. J. THOMSON, O.M., F.R.S.

My friendship with Rutherford began in October 1895 when he came up to Cambridge University as a Research Student and began at once to research at the Cavendish Laboratory. Before that time, in addition to our own students who began research after taking their degree, there had been professors and teachers at other universities who spent their Sabbatical Year in research in the Cavendish Laboratory. These were not members of the University and their work did not receive any recognition from it. In 1895 a regulation came into force by which graduates of other Universities could come up to Cambridge and become members of the University, and if after two years' residence they submitted a thesis which was declared by the referees to be of distinction as a record of original research they were enabled to receive the degree of M.A. Rutherford was the first to take advantage of this regulation, though he was only a few minutes ahead of J. S. Townsend. Rutherford was a graduate of Wellington College, New Zealand, and came over with an 1851 Exhibition. He was at that time 25 years of age, a fine, stalwart, impressive man, and he had not been more than a few weeks in the Laboratory before it was evident that he was a man of great determination and driving power. He did not require any suggestions as to the kind of research he should take up at the Laboratory, as the great majority of research students do; he brought with him his own problem which he had begun before he left New Zealand; this was an instrument for detecting wireless waves. In those early days of wireless telegraphy such instruments were neither sensitive nor very reliable. This was not altogether due to the small energy in the waves, but arose partly from the fact that the electric currents they produced in the detector were altering their directions millions of times per second. Rutherford's detector was one in which the currents going one way produced no effect while those going the opposite way did. If a piece of soft wire is magnetized to saturation, then when it is placed inside a coil through which electric currents are flowing, those flowing in one direction will not affect the magnetization while those going in the opposite direction will do so. As these experiments on wireless communication required observations to be taken simultaneously at two places, it was necessary to have at least two observers and the transport of the instruments from place to place required organization. Rutherford surmounted these difficulties by enlisting the services of his friends, and was so far successful that at one time he held the record for long-distance wireless telegraphy, having detected at the Laboratory signals which came from the Observatory about 2 miles away. An account of these researches was published in the *Transactions of the Royal Society*, vol. 189. He had not been in the Laboratory more than a few weeks before I became convinced that he was a physicist of exceptional promise, energy and strength of character. During his stay in Cambridge he was awarded the Coutts Trotter Studentship in Trinity College; it is awarded without examination, and the



From a photograph by Stearn, Cambridge

Research Students, 1899

- | | | | | | | |
|--------------|-----------------|--------------|----------------|-------------------|-------------|--------------|
| E B H Wade | G A Shakespeare | C I R Wilson | F Rutherford | W Craig-Henderson | J H Vincent | G B Bryan |
| J McClelland | C Child | P I Ingwin | I I Thomson | R S Willows | H A Wilson | J S Townsend |
| | | | I Zclery | | | |
| | | | S W Richardson | I Henry | | |

electors are instructed to pay more regard to the promise of power to carry on original research than to the amount of work already done.

Whilst Rutherford was working at his wave-detector, X rays were discovered. As soon as the discovery was announced I had a copy of Röntgen's apparatus made for the Laboratory and the first thing I did with it was to see if the X rays would make a gas through which they passed a conductor of electricity. To my great joy I found that they did even for the smallest electric forces. For more than ten years, experiments on the conduction of electricity through gases had been going on in the Laboratory, but the only way to get the electricity through the gas was to use very large electric forces and get electric sparks or to use flames; both these methods were exceedingly capricious. The X rays gave a very convenient and reliable method of making the gas a conductor. The method seemed so promising that a large number of the research workers in the Cavendish Laboratory were making experiments on this subject. Rutherford devised methods of great ingenuity and reliability, which he carried out with superb experimental skill, for determining the fundamental quantities connected with the subject, and he obtained very valuable results which helped to make the subject of conduction through gases metrical whereas before this work had been only descriptive.

Rutherford had the good fortune to begin his career as a physicist at a time perhaps unprecedented in physical discoveries of fundamental importance. A few months after the discovery of X rays, H. Becquerel found that uranium and its compounds gave out radiation which could pass through substances opaque to light, could affect a photographic plate and travelled in straight lines from its source. Shortly afterwards Schmidt found that thorium, the element next in atomic weight to uranium, possessed the same powers, but the most important discovery of all was that made by M. and Madame Curie, who discovered the new element radium which possessed these powers to an enormously greater degree than either uranium or thorium. Substances possessing these properties are said to be radioactive. The radiation was not all of the same kind, there was one kind which had comparatively small powers of penetration compared with the others; it was thought not to be deflected by magnetic forces, though Rutherford showed afterwards that it was so to an extent not comparable with the deflection produced in another type of radiation; while there was a third type of radiation which was not deflected at all by magnetic force. In 1899 Rutherford began a careful study of the three types of radiation, which he called the α , β and γ radiations, a notation which is used to this day. He began with uranium; the results he got were interesting but there was nothing fantastic about them—if you got a result one day you could get it the next. Then he took up thorium and found a very different state of affairs; it seemed as if the only results to be got were those that had never occurred before. Its behaviour seemed to be entirely frivolous, it was not affected by raising it to high temperatures or bombarding it with radiation from other radioactive substances, while opening the door of the work room produced enormous changes. Its radioactivity seemed to be contagious and infected other solid bodies in its neighbourhood. Rutherford left Cambridge in 1898 to become Professor of Physics at Montreal

and resumed his experiments on thorium. These led him to a discovery of fundamental importance, which was the origin of modern views of the processes going on in radioactive substances. The discovery was that thorium gives out not only radiations but a radioactive gas which he called an emanation; this may be wafted about, and if it settles on solid bodies makes them behave as if they were radioactive. The emanation is not permanent but after a time turns into a substance which is not radioactive. It is a very striking example of the wisdom of the policy of not leaving behind you in a research things which seem irrational according to current views.

Rutherford left Cambridge for Canada before he was eligible to sit for a Fellowship at Trinity, but when he returned to Cambridge as Cavendish Professor the College took the first opportunity of securing him as a Fellow.

§ 3. RUTHERFORD AT MCGILL UNIVERSITY

By A. NORMAN SHAW

It was fortunate for McGill University, after the departure of the brilliant Hugh L. Callendar in 1898, that John Cox, the Director of the Macdonald Physics Laboratory, was wise enough to choose Rutherford for the vacant chair. Thus at the age of twenty-seven Rutherford came to McGill University as Macdonald Professor of Physics, at about the age at which J. J. Thomson was appointed to the Cavendish chair.

The story of Rutherford's researches at McGill is one of the most impressive chapters in the history of science. Exhibiting that remarkable flair for choosing the best path to discovery, which characterized his work throughout his life, Rutherford seized on the problem of the radiations from compounds of uranium and radium. While the Curies concentrated on the chemical problems of isolating radioactive substances and determining their properties, Rutherford sought for methods of definite measurement which would reveal the physical character of the new phenomenon, and supply quantitative data concerning the behaviour of the radiations and the atoms which emitted them. In nearly all his investigations he devised ingenious direct measurements that would provide, and also test indisputably, new steps in the formation of a clearer picture or model of atomic structure and behaviour.

Throughout his life he viewed with considerable impatience the growing tendency to replace simple theoretical models or pictures and their experimental testing by an elaborate analysis and procedure designed to be as much as possible independent of all preconceived ideas. He believed that this tended to introduce unnecessary philosophical problems and difficulties, and he doubted whether a strict adherence to this procedure would be justified by greater success either in resolving obscurities of theory or in obtaining new knowledge and its fruitful application. By direct experimental attack Rutherford was able quickly to outline a simple picture concerning the new radiations. In 1899 he announced that the

radiations from these substances were of three types, which he called alpha, beta and gamma rays.

The prolific investigations on the properties of these radiations yielded a wealth of data. With the aid of pupils and collaborators, who were soon attracted from centres as far apart as England, the United States, France, Germany and Poland, papers poured out of the Macdonald Physics Laboratory for several years at the rate of nearly one a month. Of those who were attracted from abroad, many will remember Soddy, Hahn, Levin, Godlewski and Rumelin, each of whom returned to his respective country with seeds for further development and new knowledge to spread.

It was Frederick Soddy, soon to become an authority on the chemistry of the radioactive elements, who in 1903 joined with Rutherford in the brilliant unfolding of the general theory of radioactive disintegration. The constant production of fresh radioactive matter by all radioactive materials and the subsequent decay of its radioactivity, were shown to be due to the spontaneous disintegration of atoms, proceeding according to the laws of chance at such a rate that the radioactivity of a given product at any time was always proportional to the number of atoms which remained unchanged at that time. A mass of disconnected facts was soon welded into a homogeneous whole, and the evolution of whole series of radioactive substances, often differing from the parent elements in their chemical properties, was explained both qualitatively and quantitatively. Among others working actively with Rutherford at this time were H. T. Barnes, A. S. Eve, H. L. Bronson, D. McIntosh, R. B. Owens, R. W. Boyle, H. L. Cooke, R. K. McClung and Miss H. Brooks, members of the McGill staff who each made important contributions in this fascinating new field. The ability with which Rutherford got the maximum amount of work from all those around him, and at the same time imparted to them a measure of his own enthusiasm rapidly became noted, and almost every corner of the Physics Laboratory developed into a hive of continuous activity.

The important measurements of the heating effects of the new radiations were made with the collaboration of H. T. Barnes, who later occupied the Macdonald chair vacated by Rutherford, and afterwards became Director of the Laboratory (1909 to 1919). Rutherford always showed a keen interest in the well-known work on ice which Barnes was developing at that time. When Rutherford came to Montreal, Barnes was one of his first friends, and with the kindly and scholarly John Cox, who was Director of the Laboratory throughout Rutherford's period here, assisted him in his adjustments to routine duties at McGill and to the ways of our undergraduates. About 1904, A. S. Eve, afterwards another holder of the same chair and then Director of the Laboratory from 1919 to 1935, became one of the most active of Rutherford's research associates. Over twenty-five references to his work at this time are given in Rutherford's standard treatise on *Radioactivity*. Here again a warm personal friendship was established which lasted till the end of Rutherford's life.

The additional support Rutherford obtained at McGill from Sir William Macdonald in the purchase of radium and his presentation of a liquid air machine,

must not be forgotten in reviewing the conditions which made all this new work possible. In addition to the essential talent in the man, great discovery requires provision for freedom of action and protection from time-consuming routine, but without the radium and the new experimental weapons progress in this field would have been impossible. The contribution of John Cox in supporting Rutherford to the utmost and relieving him from routine, and that of Sir William Macdonald in providing first the Laboratory, second the chair, and third the special equipment, were essential factors without which the whole story would have been impossible here. The returns from these policies and investments have been truly magnificent!

To proceed with the story—to “get on with it”, as Rutherford would so often shout at the least sign of delay or interruption—the liquid-air machine enabled him to be the first to condense radium emanation (radon) and study its products and their properties. Without liquid air the production of the high vacua needed for many experiments would have been impossible at that time. Liquid air itself was a great novelty then, and in addition to its use in low-temperature work it provided the material for many entertaining demonstrations and lectures which were very popular in Montreal. Almost everyone from the Director to the janitor seems to have given liquid-air demonstrations during this period. On one occasion when liquid air was required—and it took over an hour to make a litre then—Rutherford found that the prepared supply had been taken to a church social for a demonstration, with the immediate result that the strains of “Onward, Christian Soldiers” ceased in the professor’s laboratory for some hours.

The discovery of radium A, B, C, D, and E; the discovery of radiothorium by Otto Hahn, who joined Rutherford to obtain guidance in the study of the thorium family; the early work with what turned out later to be cosmic rays, undertaken by H. L. Cooke; the measurement of the age of radioactive ores from their helium and lead content; the first studies of the collisions of alpha particles with atoms, and their resultant scattering, the beginning of the use of alpha particles as exploratory projectiles for the invasion of the atom; and experiments on ultra-violet radiations and numerous applications of the new sub-atomic physics, all added to the mountain of new material for the first edition of Rutherford’s *Radioactivity*, by far the best of his books, and to the steady stream of papers which continued till he left for Manchester in 1907.

When Rutherford was working on the detection and isolation of the numerous members of the radium family and developing the theory of the disintegration of matter, there were several occasions when colleagues in other departments gravely expressed the fear that the radical ideas about the spontaneous transmutation of matter might bring discredit on McGill University! At one long-remembered open meeting of the McGill Physical Society he was criticized in this way and advised to delay publication and proceed more cautiously; this was said seriously to the man who has probably allowed fewer errors to creep into his writings, and found it less necessary to modify what was once announced, than any other contemporary writer. At the time he was distinctly annoyed and his warm reply not entirely adequate, for in his younger days he sometimes lost his powerful command of

ready argument when faced with unreasonable or uninformed criticism. Immediately John Cox quietly rose to his support, and gave a clear review of the new ideas. Cox not only revealed incidentally his own grasp of the validity and significance of Rutherford's discoveries, but ended rhetorically with a stirring prediction that the development of radioactivity would bring a renown to McGill University by which in the future it would be widely known abroad. He ventured also to predict that some day Rutherford's experimental work would be rated as the greatest since that of Faraday—an opinion now held by the majority of those competent to judge.

The McGill Physical Society, which has been active without interruption since 1897, reached its greatest heights in Rutherford's day. The announcement of each discovery of importance was first heard there. The frequency of these discoveries, the brilliancy of the work, and the quality and value of the discussions, impressed all comers. It was there that Rutherford developed rapidly as a speaker, and after the first few years was to be heard and seen almost at his best. His clarity and direct use of simple language were coupled with dynamic ardour and contagious enthusiasm, so that even those who were unable to keep pace with the technical aspects of the subject were delighted and spellbound listeners.

Witness for example the reactions of the eloquent John MacNaughton, Professor of Classics, who has shot many a satiric dart at scientists and their doings—"plumbers" and "destroyers of art" he has sometimes called them—but Rutherford seems to have captured him in one lecture. He wrote as follows, in the *McGill University Magazine* for April, 1904: "... We paid our visit to the Physical Society. Fortune favoured us beyond our deserts. We found that we had stumbled in upon one of Dr Rutherford's brilliant demonstrations of radium. It was indeed an eye-opener. The lecturer himself seemed like a large piece of the expensive and marvellous substance he was describing. Radioactive is the one sufficient term to characterize the total impression made upon us by his personality. Emanations of light and energy, swift and penetrating, cathode rays strong enough to pierce a brick wall, or the head of a professor of literature, appeared to sparkle and coruscate from him all over in sheaves. Here was the rarest and most refreshing spectacle—the pure ardour of the chase, a man quite possessed by a noble work and altogether happy in it."

When the assurance is recalled with which Rutherford discussed the major problems of physics in learned societies, and the ability with which he handled men, it is surprising to remember that as a young man he was a nervous lecturer, particularly when dealing with elementary topics for undergraduates. His lectures on electricity and magnetism to large classes of second-year engineering and arts students at McGill were at first above the heads of the students, and revealed a feeling of despair in regard to the previous mathematical and scientific training of his class. Those of his students who were interested in physics, however, caught something of the fire with which he inspired all his advanced students and collaborators. They learned the importance of striving to build their knowledge on fundamental principles established by experiment and to achieve the ability to

apply these principles and to reason about them. Any attempts to concentrate mainly on definitions and isolated facts, and to rely primarily on memory, he roundly condemned. His scorn at the memorizing of electrical formulae, imagined by many students then as now to be a necessary part of the process of learning, will never be forgotten by students in his classes who pinned their faith on memory.

Before he left Montreal in 1907, at the age of thirty-six, he had already been elected Fellow of the Royal Society of Canada (1900) and Fellow of the Royal Society of London (1903), awarded the Rumford Medal (1904), appointed Bakerian Lecturer at the Royal Society (1904) and Silliman Lecturer at Yale (1905), elected President of Section III in the Royal Society of Canada (1906), and received honorary degrees from the universities of New Zealand (1901), Pennsylvania (1906), Wisconsin (1906) and McGill (1907). Before leaving he had already been slated for the Nobel Prize in Chemistry (\$40,000), which was awarded to him in 1908. He was given the chemistry award because the Nobel Committee classified the new phenomena of atom-changing as chemical by definition.

The debt of Canada to Lord Rutherford is beyond assessment. Undoubtedly the greatest outburst of original discovery that has occurred in Canada was entirely due to his leadership. Its subsequent influence affected all walks of science in the country, speeding the growing demand for higher scientific training and investigation. For almost the first time, Canadians began to understand that the scientific developments of modern civilization had been made possible primarily by workers and thinkers of the Rutherford type. The methods of scientific thinking and procedure attracted more attention as an immediate result of his spectacular achievements, and the vital demand for more research and scientific method in universities, in industry, and in national enterprises was greatly strengthened. The standards of our youthful Canadian Royal Society, the quality of scientific work in government departments, and the conduct of higher training in our universities were in turn the targets of his constructive criticism, for in spite of his indefatigable labours in the laboratory, he rarely missed an opportunity to promote the spread of science and its methods of thought and procedure.

§ 4. RUTHERFORD IN MANCHESTER, 1907-1919

By Prof. H. R. ROBINSON, F.R.S.

Rutherford, as Langworthy Professor of Physics and Director of the Physical Laboratories, served the Victoria University of Manchester for nearly twelve years, and these, in spite of the abnormal conditions of the last five of them, were among the most fruitful years of his scientific life. The work he did in these years has long been incorporated in the standard literature of physics, and it will be familiar, at least in outline, to all readers of these *Proceedings*, even to those who have not specialized in radioactivity or its later development, nuclear physics. There is therefore no point in attempting here a detailed survey of his scientific work in Manchester; no more is needed than a very brief account, sufficient to show which



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of Rutherford's major contributions to science were associated with the Manchester laboratory, and to indicate the main features of the work which he did and directed there. Similarly, no attempt will be made to mention by name all the members of the research school which he built up in Manchester in the years before the War. I found it easy to write down from memory more than 40 names of workers belonging to that period; in what follows, only a few of these names will be mentioned and these will not necessarily be the most important ones. It must be understood that many of those omitted are at least as distinguished as many of those included; in fact, with better cause than Ruy Gomez, I am compelled to say "J'en passe, et des meilleurs". On the other hand, the more personal and—if we may so call them—the more domestic details of Rutherford's life in the Manchester laboratory are not to be found in the scientific literature; an attempt—necessarily incomplete and one-sided—will therefore be made in the following pages to recapture some of these.

Almost immediately after he arrived from McGill, Rutherford began, with Geiger, the beautiful and now classical experiments in which individual α particles were detected by their electrical effects. The results of this work, in which in effect an almost direct count was made of the number of α particles emitted per second by a gramme of radium, were published in 1908. From them it was possible to calculate a number of important constants, and when they were combined with the known rate of production of helium gas in radium salts, they yielded the most direct determination imaginable of Avogadro's number. At the same time, Rutherford and Geiger measured the total charge carried away in a given time by the α particles from a radioactive source of known strength. By combining this result with that of the counting experiments they were able to show that the α particle was doubly charged, and to deduce a trustworthy value for the electronic charge.

In the following year Rutherford obtained, with Royds, complete spectroscopic proof of the identity of the α particle with helium. A point to be noticed here is the concentration of Rutherford's interest at this stage on the properties of the α particles. The work at McGill had fully established the validity of the disintegration theory, and the sequences of changes in the active deposits of radium, thorium and actinium had been fairly completely elucidated, so Rutherford's main interests naturally turned to the properties of the radiations, and in particular to those of α particles. His interest in the radioactive families was revived later by the discovery in his laboratory of short-lived members of the actinium and thorium series, and of the branching which was found to occur in all the three main series, but it was on the radiations that he did most of his work after 1907. There is a deep significance in the changes of title in his books—from *Radioactivity* in 1904 and 1905 to *Radioactive Substances and their Radiations* in 1912 and the *Radiations from Radioactive Substances* of Rutherford, Chadwick and Ellis in 1930.

Other work on, or nearly related to, the properties of the α particles in which Rutherford took an active and personal part during the pre-war period in Manchester included the accurate measurement (with Robinson) of the specific charge

and velocities of the particles, and of the variation with time of the heating effect of the active deposit of radium. At the same time, a great deal of important work was going on under his general direction; of this, we need only mention Geiger and Nuttall's measurements of the ranges of the particles from different elements, which were summarized in the well-known Geiger-Nuttall relation between range and transformation constant. The work which had the most profound influence on the later development of the subject—that on the scattering of the α particles—was begun by Geiger in 1908 and continued in association with Marsden from 1909 onwards. Further reference to this will be deferred for the moment.

Rutherford also had many people in the laboratory at work on β -ray problems, and one of Moseley's first researches was a determination of the number of particles emitted in β disintegrations. Rutherford himself did not take a particularly active part in β -ray work until after he had put forward the nuclear theory of the atom. He then recognized the possibility of obtaining information on atomic structure from a study of the β rays, and with Robinson he investigated in 1913 the β -ray spectra of radium B and C. Later, with Robinson and Rawlinson, he began a similar investigation of secondary β -ray spectra, but this was interrupted in 1914.

About the same time, and for similar reasons, he developed a stronger interest in the γ radiations. Much important and intricate work had already been done in the laboratory by Gray, Florance and others, and Rutherford had himself collaborated with Chadwick in a γ -ray research. About 1912 he began a large-scale attack upon the difficult problem of analysing the γ radiations from a number of radioactive bodies, at first, with Richardson and others, by absorption methods. In 1913, with Andrade, who had just come to Manchester as John Harling Fellow in the University, he measured a number of γ -ray wave-lengths by the newly discovered method of reflection from crystal faces. The transmission method of using the crystal was invented in the course of this work.

Rutherford's greatest single contribution to physical science was based on an apparently minor detail which emerged from the α -particle scattering experiments of Geiger and Marsden. It had been found by these workers that when a pencil of α particles passed through a thin metal foil—a foil so thin that the average angle of scattering was no more than a degree or two—a quite unexpectedly large fraction of the particles (roughly one in 10,000) experienced deflections of more than a right angle. Rutherford's brilliant solution of the problems raised by this observation—his nuclear theory of atomic structure—was published in 1911 (*Phil. Mag.* **21**, 669). In this paper he worked out fully the laws of single scattering of α particles by a nuclear atom, and his deductions were quantitatively verified in further experiments by Geiger and Marsden.

The next two significant advances in nuclear theory had their origins under the direct influence of Rutherford. In 1913 Bohr showed that if certain quantum principles were applied in the description of the motions of the extranuclear electrons, Rutherford's atom-model could be made to lead to a quantitative explanation of known regularities in optical line-spectra. In the same year Moseley, in an equally brilliant experimental research, was able to show how X-ray spectra

depended upon nuclear charge, and to establish the importance and precise significance of the concept of *atomic number*. Bohr's three papers on "the constitution of atoms and molecules" and Moseley's first paper on "the high-frequency spectra of the elements" were all communicated by Rutherford to the *Philosophical Magazine*, and they appeared respectively in the numbers of that journal for July, August, September and December, 1913.

Before the lines of research opened up by these new discoveries could be at all fully exploited, war was declared, and Rutherford's research school was almost completely broken up. He carried on research with the remnants of his school, but more and more of his time was taken for official war work, and though he had in Evans an exceptionally good and capable senior lecturer, it was difficult to carry on the routine work of the Department with a staff so heavily depleted. Most men would have found it impossible to do creative work under these conditions, and it is characteristic of Rutherford's energy and enthusiasm that he should have emerged, only a few weeks after the Armistice, with an experimental research of the very highest importance. This was the work, published in the *Philosophical Magazine* for June, 1919, in which he showed from beautiful experiments, strictly controlled, that the nitrogen nucleus could be artificially disintegrated by the impact of fast α particles, and that a fast proton was one of the products of the disintegration. At this time there were practically no research students in the laboratory, and Rutherford enlisted his laboratory steward, Kay, to help in counting scintillations. This was the last work he published before he left for Cambridge, and it was the starting point of a whole series of brilliant investigations.

It is now time to say something of the laboratory which, as we have seen, saw the birth of the nuclear atom and the first experiments on artificial disintegration of the elements. The Manchester University Physical Laboratory had been designed with great care by Rutherford's immediate predecessor, Arthur Schuster, who was a very fine physicist and something of a pioneer in organized physical laboratory instruction. The laboratories were nearly new (they had been opened in 1900) and they were well equipped for electrical work. Further, there was a good electrical engineering department, which a few years later became an independent department under the control of Professor R. Beattie, but which was in 1907 at least nominally a part of the department of physics, and was housed in the same building. This arrangement was of immense advantage to the physics department, as it made it possible to have instruments for research quickly and accurately calibrated, and Beattie and his staff were always most helpful with advice on problems of electrical measurement and equipment.

The laboratory also had a liquid-air machine and—perhaps even rarer at that time, and certainly more important—a laboratory steward, William Kay, who could be relied upon to make it work whenever liquid air was required. Rutherford therefore came to laboratories which were very suitable for research in radioactivity. He brought some radium with him, and later the Austrian Government, recognizing the importance of his work, lent him a larger supply—about 450 milligrammes of radium bromide—with which much of his Manchester work was done. Geiger,

who was already in Manchester—he had started work there with Schuster—was immediately taken into working partnership, and soon became Rutherford's right-hand man, and unofficially a sort of assistant director of radioactive research.

Rutherford was not overburdened with administrative or teaching duties, and he was helped when he came to Manchester by a young and enthusiastic assistant staff, with whom he was immediately on the best of terms. Most of the members of his staff took part in radioactive research, and W. Makower (Senior Lecturer, and later Assistant Director of the Laboratories) collaborated with Geiger in a textbook on experimental radioactivity which was based on the course of instruction developed in the Manchester laboratory. Rutherford was also fortunate in his colleagues outside the physics department. In particular, he found in Horace Lamb, the distinguished head of the mathematical department, a very good friend and a wise counsellor in matters of University politics.

Rutherford then slipped easily and comfortably into life and work in Manchester. Manchester liked him at sight, and he gave every appearance of liking Manchester. This certainly meant that he did like Manchester, for he was never very gifted (or even assiduous) in concealing his dislikes.

His post at McGill had been a research professorship, and I imagine that he had done little formal lecturing to degree students before he came to Manchester. In my time as a student, he lectured only to the elementary (Intermediate) class and on electromagnetism to the second-year honours class. Technically, I suppose that he was not a very good lecturer—that is, he had none of the arts of the trained orator, and he sometimes got his sentences oddly twisted up when he embarked too eagerly on the explanation of something that interested him very much—but he was the most inspiring lecturer I have ever heard, and he was blessed with a naturally good and pleasing voice. Although it was no part of their official course, the honours students used always to attend his Intermediate lectures. This was no doubt partly because the lectures were good fun—Kay loved to devise and set up elaborate and beautiful experiments, and Rutherford loved to show them; it was in fact sometimes said that the lecture course was largely dictated by Kay—that Kay set out the experiments he thought appropriate to the time of year, and Rutherford came in, looked round the lecture bench, and lectured on whatever he found there. The real appeal of Rutherford's lectures to the better students was, however, due to his extraordinary gift of seeing the essential *physics* in any problem, and imparting it to his hearers; even if a man already knew a good deal about the subject matter of one of Rutherford's lectures, he was bound to get a new, and sometimes dazzling, light upon some aspect of it after it had passed through Rutherford's mind. In later years this gift was made apparent to much wider audiences, and it is probably very generally known to-day; I stress it specially here because it was an important factor in Rutherford's outstanding success as a teacher in Manchester. His more advanced lectures, and especially his lectures on his own subject, were a pure delight. Moreover, it should be noted that Rutherford took teaching as a serious responsibility—in spite of his own devotion to research, he had no patience with the

type which affects to regard the efficient teaching of students as an inferior, or even degrading and time-wasting, function of a University teacher.

It was, however, in the research laboratories that his influence was most apparent. He soon filled—and over-filled—them with workers from all over the world, leavened as time went on with a good proportion of students of his own training. He continued, with no apparent effort, to find space, apparatus and ideas for research for this large team, and yet to do a great deal of experimental work with his own hands. The problem of finding space was simplified a few years later, by the provision of additional accommodation, but the apparatus problem must always have been fairly serious, as it is unlikely that his departmental grant could ever have kept pace with so rapidly expanding a volume of experimental work. That this problem was solved at all, can only be attributed to Rutherford's genius for devising simple and effective experimental methods. The magnitude of the laboratory's output of experimental research was not so much due to the possession of large financial and technical resources, as to Rutherford's amazing fertility in ideas for new experiments. In a large proportion of the ionization measurements made in the earlier years in Manchester, the only electroscopes used were made from discarded cigarette tins. A Fleuss pump had to serve many masters, and was dragged from room to room as required; in my first work with Rutherford on β -ray spectra, we used to evacuate the whole apparatus from scratch with a hand-operated Toepler pump—and I remember that Rutherford taught me to use the pump in the dark, judging the stage in the cycle of pumping operations by the "feel" of the mercury reservoir in the hands.

In assessing the magnitude of Rutherford's personal contribution to science during this period, it should be kept in mind that he was extraordinarily generous as a collaborator in, and director of, research. If his name appeared on a joint paper, it meant that he had taken a large personal share in the experimental work, and many papers on which his name did not appear were full of ideas which he had freely given. He spent a great deal of time in going round the laboratories and discussing with each research worker his results and difficulties. The magnitude of the published work which bears his name, impressive though that is, falls far short of his *effective* output.

His genius as an experimenter and his skill with apparatus were fully appreciated by his school in Manchester. It was strongly held in the laboratory that he could take liberties with apparatus which would inevitably have been disastrous if attempted by lesser men. It is certainly true that he practically never broke anything; it was at times almost exasperating after one had been struggling, for instance, for ten minutes to coax along a mercury pellet that was blocking some narrow section of an elaborate and fragile system of glass tubing, to see Rutherford come breezily in, hit a tube really hard at exactly the right point, and send the mercury scuttling obediently to its appointed place. Yet, in spite of his own skill, he was wonderfully tolerant of the effects of clumsiness in others, unless he suspected that there had been real carelessness. He found it difficult to forgive anyone who admitted mercury to the barrel of a Fleuss pump.

After this, I cannot resist the temptation to tell the story, with its very characteristic sequel, of an isolated instance in which Rutherford's hand showed less than its usual cunning. There was a rather elaborate pumping train that was used for collecting and purifying radon, and one day I found a connecting tube cracked right across at a point very close to a stopcock. This tube joined two quite heavy pieces of apparatus, each standing in its own mercury tray; the glass was probably rotten through prolonged exposure to radon, and the nearness of the crack to the stopcock made an effective repair almost impossible. An experienced glassblower would have condemned the section at once, but as I knew too little to realize all the difficulties, I tried to join the two broken ends. As it happened, I had beginner's luck; I got the joint almost completed, and, with the glass nicely flowing, I was just adding the finishing touches with a spicule of patching glass when Rutherford came in. This, of course, was a sight he could not resist, "Ha!" he said, "you want them closer together", and he pushed one of the trays towards the other. Unfortunately, the apparatus being heavy and the floor not very smooth, the tray came in a good two inches once it had begun to move, and the joint was ruined beyond redemption.

Rutherford at once realized the extent of the calamity, and exerted himself to cheer me—"I'm terribly sorry; I know how annoying it is—of course I used to do a *lot* of glass-blowing myself when I was younger." No doubt I visibly pricked up my ears at this, and Rutherford, pleased with his effect, went on: "I used to make X-ray tubes—lots of 'em!"—then, realizing that he'd been carried too far, he hastily added, with a characteristic twinkle: "Only little ones, of course!"

Rutherford's phenomenal memory was another source of pride, and sometimes of amusement, to his Department. He appeared to have a sort of mental card-index of all the more useful measuring instruments in the laboratory—certainly of all the good ammeters and voltmeters—and I think that when Beattie took the Electrical Engineering Department over into new quarters he had some difficulty in getting away with his own materials. But Rutherford not only remembered permanent apparatus—he seemed to remember every tube that had been filled with radon. If somebody wanted a supply of radium D-E-F, and the old radon tubes were being collected, he would say, "What about that 100 millicuries that Makower and Moseley had?"—referring to some source which had been given out perhaps two years earlier. His research assistant knew that even if he did not immediately report the accidental destruction or loss of a radon tube, there was no chance of its remaining undiscovered for long.

Rutherford was, of course, first and always an experimenter, and an experimenter with an uncanny knack of knowing just what experiment ought to be tried, and how to set about it. It has often enough been said that he was no mathematician, but this has most often been said by men with far less real mathematical sense than he had. It is obvious that his mathematical attainments were less, for instance, than those of his predecessors in the Cavendish chair, but as Professor Eve has recently pointed out, if he really needed a piece of mathematics he could generally produce it. Eve made this remark in connexion with Rutherford's first

handling of the equations of radioactive transformation, and I can recall other instances. When, for example, we were measuring the ratio E/M of the α particle, we took photographs of the electrostatic and magnetic deflections of the three groups (radon, radium A and C) of particles from a radon source contained in a glass α -ray tube. We measured the plates one afternoon, and made a hasty calculation of the results. Even a rough calculation sufficed to show clearly that the three groups gave markedly different values for the specific charge, and there was no obvious explanation. We went home in rather chastened mood to think it over, and Rutherford arrived early next morning with a complete and elegant solution, which he had obtained overnight. It was not a very simple problem, but he had succeeded in showing that the explanation lay in the retardations experienced by the particles in traversing the walls of the α -ray tube. Particles of a given velocity were less retarded if they passed through nearly normally than if they passed through obliquely, and the resulting differences in velocity on emergence gave rise to a displacement on the photographic plate of the centre of gravity of the deflected pencil. Rutherford had worked out the full theory of this effect, and when we re-measured the plates in the light of his calculations, measuring to the edges and not to the centres of the displaced lines, we found agreement to within 1 part in 1000, in place of discrepancies of over 1 per cent. Again, the semicircular focusing method which we used for β -ray spectra was not essentially new, but I think that Rutherford was the first to see clearly the underlying principle, and to exploit it fully. Mathematician or no mathematician, he had a very sound geometrical instinct, and with a little trouble I think he could have beaten many professed mathematicians at their own game.

In the Manchester laboratory, any really heavy mathematical work could be handled by the Reader in Mathematical Physics. The readers in Rutherford's time were Bateman, Darwin and Bohr, all of whom made contributions to radioactive theory. Darwin and Bohr made notable contributions to the theory of the passage of α and β particles through matter, and Bateman put the transformation equations into a more symmetrical form. The readership, instituted through the generosity and foresight of Schuster, was a most valuable addition to the all-round strength of the Department—and I think the readers would readily admit that for their part they gained a great deal by being brought into contact with Rutherford and the problems which his work provided. Darwin, indeed, was so moved by the spirit of the place that he began experimental research in radioactivity. Later he became interested in X rays, and besides making a classical contribution to the theory of X-ray reflection he did experimental research with Moseley and independently.

Rutherford's personal relations with his colleagues and students were of the happiest. Much may often be learned from a man's nickname, and Rutherford's in Manchester ("Papa") was a mark of sincere affection.

He ruled in the laboratory as a benevolent despot, and he knew exactly how to get the best amount of work out of every member of his sometimes oddly assorted team of research workers. The main reason for his success in this was that he was

leading his team rather than driving it. Perhaps he did drive it a little—it would be idle to deny that there was sometimes a slight, but conscious, slackening of effort on those Thursdays when he was known to be reading a paper to the Royal Society—but he did not over-drive. He did not bully, and it was not in him to nag. People who worked hard for him did so largely because he was so obviously eager to know the results of their work; even if a man had no great inward stimulus to the work on which he was engaged, he was sure to be caught by something of Rutherford's enthusiasm. Sometimes the excited activity was of short duration, but often it endured.

Rutherford's attitude to long hours in the laboratory was charmingly inconsistent. Officially he was opposed to late night work—but he had a habit of leaving the laboratory about seven, and on his arrival next morning at nine asking how the work had gone in the meantime. Further, it was not unknown for him to look in quite late—perhaps while driving back with Lady Rutherford from the theatre—to see how things were going on. But he was very quick in applying the stopper if he thought anyone was beginning to show signs of overwork.

His interest in his students and their well-being was not confined to the laboratory. He and Lady Rutherford entertained a great deal, and at their house in Withington the research students made a number of outside contacts, with members of other University departments, with guests from outside, and with visitors from abroad. This was all to the good, as the research school was a large and happy family, and it might well have tended to become too self-contained and self-centred a unit. There was a lot of interesting gossip at the Sunday evening gatherings in the Rutherfords' house, and it was part of a liberal education to hear, for instance, Rutherford and Lamb together in reminiscent mood. Lamb's interests had always been largely in the more physical side of his subject; he was much the older man, and his recollections went back to the time of Maxwell. Lamb was less easily than Rutherford lured into verbal indiscretion, but he had a strong sense of humour and a very shrewd judgment, and in his company Rutherford was always at his best and most entertaining. "Shop" was not, of course, by any means the sole topic of conversation, but a great deal of informal knowledge of physics—and physicists—was to be picked up on such occasions as this.

Rutherford had a genius for easy friendship with young and old alike. His immense vitality and unaffected, buoyant good-nature won him friends everywhere, and he made a wide, deep and lasting impression in Manchester. As one of the oldest and reputedly the most crabbed of the University officials said to me just after he had left for Cambridge: "Your Chief was like a breath of fresh air about the place." At any meeting of any of his old students or colleagues almost the first words were sure to be "Seen or heard anything of Rutherford lately?"—and so long as any of us survive, his memory will always be green.

§ 5. THE CAVENDISH CHAIR

By Prof. C. D. ELLIS, F.R.S.

Rutherford came to Cambridge in 1919, and to-day the Cavendish Laboratory represents his work done in the intervening years. The Laboratory was his greatest experiment, and like the apparatus in an experiment it grew organically with but little planning. Had he lived we should have seen the results of this great experiment put into permanent form, and no one who knew Rutherford can doubt that it would have carried the stamp of his personality. But the experimenter is dead and the experiment is to be completed by others. It is the fate of all great men to leave unfinished work, and not the least of the tragedies associated with Rutherford's death is that he could not have been spared to rebuild his laboratory and fit it for many years to come to carry on his traditions.

Rutherford's work at Cambridge is well known and a full description would mean recounting the development of nuclear physics in the last two decades. This is not the occasion to attempt that task, and just a few recollections of his personal experiments seem most fitting. Soon after he came to Cambridge he found the time to follow up vigorously the experiments on the artificial disintegration of the light elements which he had started during the war period. In those days the experiments still involved only simple apparatus and were of the type Rutherford loved. A radioactive source provided the α particles which fell on a foil of the material to be disintegrated, and the resulting protons, hitting a zinc sulphide screen, were detected by the scintillation method. The whole apparatus was contained in a small brass box and the scintillations were viewed with a microscope. I can well remember being surprised, in fact mildly shocked, that the apparatus was not more impressive, yet these experiments, so simple on the surface, required the highest experimental skill to make them yield dependable results.

Counting the scintillations was difficult and tiring, and Rutherford usually had one or two of his research students to help him. The experiments started at about four in the afternoon and we went into his laboratory to spend a preliminary half an hour in the dark to get our eyes into the sensitive state necessary for counting. Sitting there, drinking tea, in the dim light of a minute gas jet at the further end of the laboratory, we listened to Rutherford talking of all things under the sun. It was curiously intimate but yet impersonal and all of it coloured by that characteristic of his of considering statements independently of the person who put them forward.

Soon his assistant Crowe would appear with the radioactive source, which had required long and careful preparation, and while the lights were turned up for him to fix it in the apparatus, the counters and Rutherford would either keep their eyes tightly closed or huddle into a little wooden shed built in one corner. Then counting would start, each in turn taking his place at the microscope for a minute. It was very striking how Rutherford could keep entire control of the experiment. Working in comparative darkness, with no time to waste since the radioactive source was

decaying, he would sum up instantly the implications of the results and issue his directions. The secret, I am sure, was that he thought so deeply about the experiments that he had already anticipated the results before he started. All the relevant quantities were calculated in advance and he detected instantly the first indication that something unexpected was happening. He was the complete antithesis of the man who observes first and then goes home to work up the measurements to find out what has happened. As the scintillations were recorded Rutherford compared them with what he expected and translated them at once into the final deductions from the experiment. Sometimes, only too frequently, the dreaded contamination would occur. Despite all precautions some of the radioactive material would become detached from the source and reach a part of the apparatus from where the primary α particles could reach the scintillation screen. In no uncertain way Rutherford would express his feelings, there was no question of detached philosophic calm, his attitude to the experiments was far too human and personal for that.

As time went on the experiments became more and more laborious and progress slower, and despite the brilliant results obtained by Rutherford and Chadwick by these methods it was clear that the limit was being reached. He therefore initiated investigations on the possibility of using electrical methods of counting. Eventually, owing to the able work of Wynn-Williams, these were brought to an efficient and dependable state and he returned once more to his beloved α particles. He saw that these new methods were capable of supplying far more detail than had been obtainable by the older technique, and both by his own experiments and by those of others in his laboratory he led a new investigation of the nuclear structure of the heavy radioactive elements. It was towards the end of this period that there came the discovery of the disintegration of the light elements by protons, of the neutron, and of induced radioactivity. Rutherford's personal experiments, now in collaboration with Oliphant, were on the disintegration of the light elements by protons and deuterons by means of relatively slow particles, whose poor efficiency was offset by the intensity of the beam. This is all recent history and his work in this field is well known. Had he lived he would have turned his attention to the use of the fast particles produced in the new high-voltage laboratory he had planned and developed.

Rutherford had a genius for working in the right direction. Any competent experimenter could have done most of his work, but anyone except Rutherford would have strayed from the path. The extent of his advances is due primarily to the fact that he went forward in a straight line, and had that deep insight which told him when a reasonable experiment was only really a side line; when a certain measurement, though important, could yet afford to be left a while; and when, although good experiments were waiting, they were not really progressive and it was the moment to abandon old methods and develop new technique. While he was always striving to develop technique, I believe that he regretted the passing of the old simple and direct experiments, and as the apparatus became more and more complicated, so the experiments became less personal, and the final results became more remote and only obtainable after analysis when the experiments had long been finished. He loved lecture demonstrations, when, despite the complica-

tion of the apparatus, he could produce instant and visible effects of the fundamental phenomenon.

Perhaps the most characteristic example of his genius during his Cambridge period is to be found in a paper, *Phil. Mag.* 4, 580 (1927), which at the time made little impression and is now almost forgotten. It puts forward a theory about the origin of the α particles, and the details of this type of disintegration, which was soon completely superseded by the wave-mechanical picture. Yet what is so interesting is that it shows how completely he had appreciated the difficulties that lay in the way of any explanation on classical lines. From his own experiments on the scattering of α particles and from those carried out in collaboration with Chadwick, he became convinced that the inverse-square electric field round a heavy nucleus must be valid to such small distances that the potential energy of a nucleus and α particle could reach values of ten million electron-volts. Even if an α particle, by some mechanism, just trickled away from the attraction of the main nucleus, it would find itself in this strong repulsive field, and could not possibly emerge from the atom with kinetic energy less than ten million volts. Yet the α particles from uranium have energies of less than six million electron-volts. The hypothesis he suggested to overcome this difficulty is to-day unimportant, but the fact on which he based his argument is recognized to be one of the crucial points which show the need for some theory other than classical mechanics in dealing with these matters. Rutherford's ability to seize on one definite fact, to realize that independently of all other arguments it showed a fundamental error in the current physical picture, and then to follow this trail wherever it led, this ability was the measure of his genius. It is shown no less strikingly in this example than in his famous deduction from the fact that α particles could very occasionally be scattered through large angles. In the latter case he found the right answer, in the former he did not, but the real achievement was the realization of the experimental fact and insistence on its importance.

It is impossible to describe the work of all the people who worked in his laboratory. The majority of the experiments were really started by his direct or indirect suggestion, although he was always willing to let anyone go his own way, and in fact invariably asked for suggestions both from the permanent members of the laboratory and from newcomers. Even in the later years when he had so many outside responsibilities he took a deep and personal interest in all the researches and stimulated all stages of the work to a remarkable degree. His grasp of the implications and true interest of the experiments was extraordinary, but it was by no means always immediately apparent. He would come round to see what was happening and frequently the conversation became positively awkward because he would talk so vaguely and confuse all the relevant terms to such a degree that it was difficult to avoid correcting him, a step not lightly to be undertaken. He would leave and one would reflect on what a remarkably clear grasp one had of the problem. In fact so clearly did one see what was the next step to take and what lay beyond, that really the only thing to do was to see Rutherford and tell him about it properly. Then as one arranged one's thoughts would slowly come the conviction that this

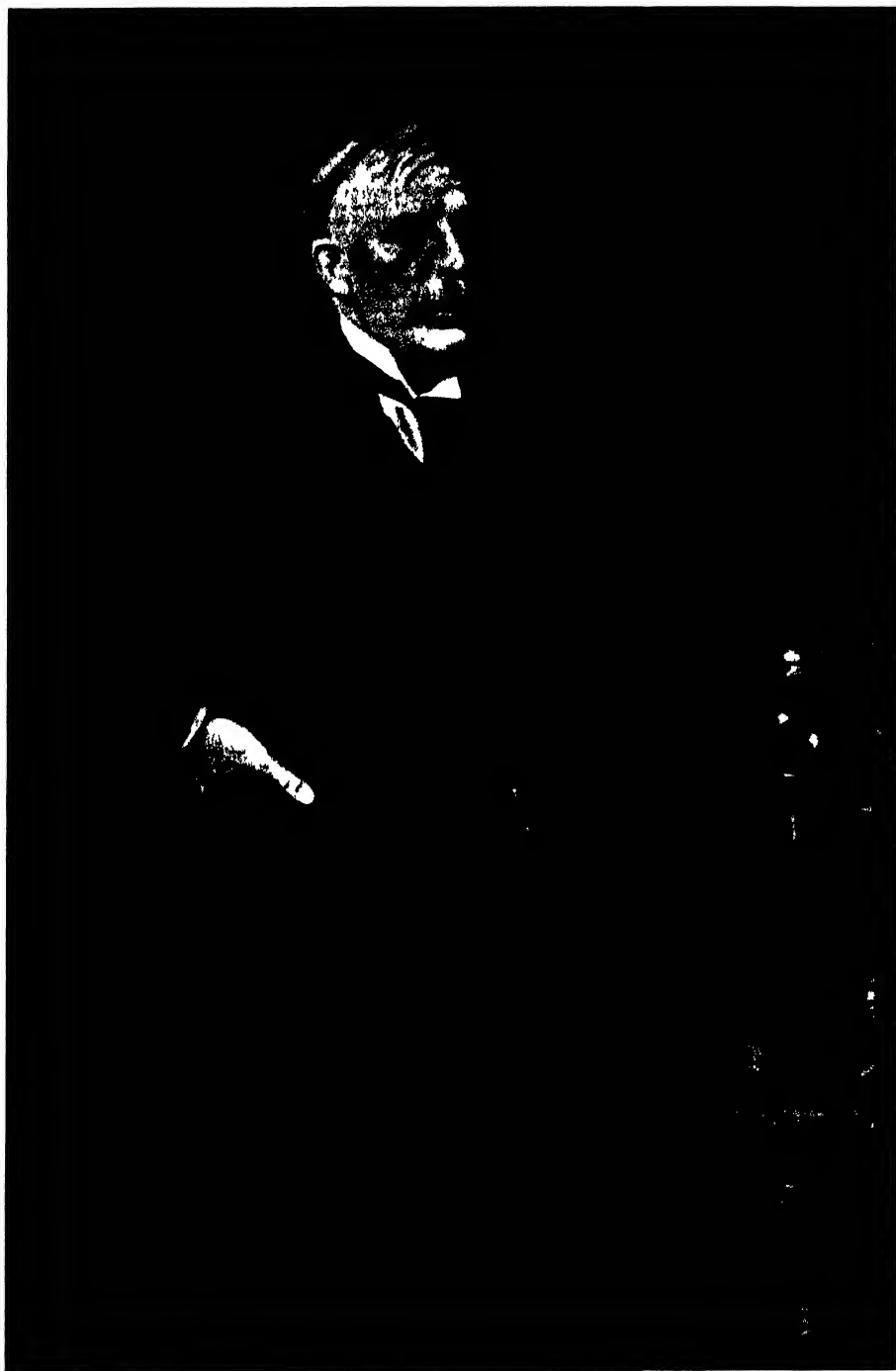
was just what he had been saying, that he had seen it all far more precisely and that this wonderful new idea was only the slow working of his inspiration. He had such a simple outlook, so unbiased by current theoretical ideas, that it was difficult to appreciate immediately all that he meant just because it was so direct and so simple. He did not think logically, it would be far more just to say that he had an artistic feeling of the way nature works. It was always so clear to him what was the next thing to do that he neither would give reasons for it nor felt the need to do so, he did not in fact appear to be greatly interested in what current theory might have to say for or against his ideas. To the end he was unappreciative of quantum mechanics, and had little use for the wave picture. Particles were particles and that was the end of it.

At the beginning of every Michaelmas term he would speak at the first meeting of the Cavendish Society and give a review of those advances of the past year in which he had been particularly interested. He obviously enjoyed this occasion when, to use his own phrase, he told the boys all about it, and his enthusiasm and conviction of the importance of the work were clear to every one. He was a natural leader, not because he particularly wanted to dominate but because he was completely sure that he was doing the right thing and intended to go on doing it. Other people who followed him were obviously sensible; if they did not follow him, he did not attempt to force them but he had the gravest doubts about their wisdom.

Rutherford bore his share of university and college administrative duties, and served on many important committees. I think he did not like the committee method of administration and found the work rather tiresome. He never really appreciated the essential democracy of Cambridge, although he of all men was, in some senses, the most democratic. He was just as likely to tell some important and distinguished person what an unimportant person had said as vice versa, in fact these distinctions did not exist for him. Yet anything that impeded the fulfilment of what was to him the obvious thing made him impatient, and it was an interesting example of restraint to hear him putting forward a persuasive argument at a board in favour of a project when he had already made up his mind that it was going to be realized.

He used to dine at Trinity on most Sundays, and fairly frequently once or twice during the week. He had not much use for fine wines and frankly confessed his lack of appreciation. What he wanted after dinner was a pipe and rarely did he go to the Combination Room on ordinary nights. In the smoking room, by the force of his joviality and humanity, he usually gathered round him a group of people who would be discussing anything except physics. He was at his best when discussing incidents from his early days. Interested in people, and with a tenacious memory, he would recount events and conversations in such a vivid manner that he could hold the interest of any group of people.

Towards the end of his time at Cambridge he was increasingly occupied with outside responsibilities, but yet he kept absolute control of his laboratory. In that large rambling collection of buildings his personality was everywhere. It is still the Cavendish Laboratory but it is no longer Rutherford's Laboratory.



Photograph of the portrait painted by Oswald Birley

**SIR HERBERT JACKSON, K.B.E., F.R.S., Emeritus Professor
of Chemistry in the University of London**

1863-1936

SIR HERBERT JACKSON died, after a short and painless illness, at Parsifal Road, Hampstead, on 10 December 1936, in his 74th year. He was born on 17 March 1863 on the Surrey side of London and came of a family which had its origins, or some of them, in Yorkshire. However, he lived nearly all of the earlier and most of the later part of his life in Hampstead. He was educated at King's College School until he entered King's College, where he worked as student, Daniell Scholar and Student Demonstrator under Professor C. L. Bloxam, much of his work being done in Professor Bloxam's private laboratory. He was appointed Lecturer in Chemistry soon after John Millar Thomson had succeeded Bloxam as Daniell Professor in 1879, became Assistant Professor in 1902 and Professor of Organic Chemistry in 1905. He was elected a Fellow of King's College in 1907 and appointed Daniell Professor of Chemistry in succession to Thomson in 1914. He resigned this position in 1918, with the title of Emeritus Professor of Chemistry in the University of London, on his appointment as Director of Research of the British Scientific Instrument Research Association, a position which he held until 1933, afterwards acting as consultant to the Association and as a member of its Research Committee.

As a young man Jackson was a good all-round athlete with notable or creditable achievements in such varied directions as running, Rugby football (in this field he was regarded as a possible England cap), step-dancing and boxing, among others. Throughout the period (nearly 40 years) during which he was associated with King's College he took part in the annual sports either as competitor, as judge, or in some other capacity on almost every occasion. However, the writer is compelled to add that he took a share or an interest in almost every activity, of whatever kind, of any importance which was connected with the College.

A great difficulty in writing an account of Jackson's scientific work arises from the paucity of his publications. These are few and quite inadequate and out of proportion to the immense output of experimental investigation he accomplished. A very fluent talker and an excellent and facile experimenter, he seems to have found writing either burdensome or distasteful. In 1883-4 he contributed three notes to the Chemical Society on "The action of sulphuric acid upon potassium iodide", "Bromine as a test for strychnine" and "The action of arsenious anhydride on glycerol".

In or about 1890 Jackson began a remarkable and extensive series of investigations on phosphorescence. These included the production of fluorescent and phosphorescent materials, their behaviour when excited by ultra-violet light and by exposure to electric discharges in low and high vacuum discharge tubes, and the effect of the form of the glass envelope and of the shape and position of the electrodes on the resulting phosphorescence. During these experiments he discovered that in a high-vacuum discharge from a concave cathode of uniform curvature the excitation

of the phosphorescent material used as anticathode could be confined to a small area about the centre of curvature of the cathode. In some cases the phosphorescent substance became appreciably heated over this area. It will be recalled that similar observations had been made upon other materials by Crookes in 1874 to 1879. Some of Jackson's tubes had anticathodes made of various non-phosphorescent substances, including metals, to find out whether such materials emitted invisible phosphorescent radiations when excited in an electric discharge tube. Jackson made all his own tubes and did all his own glass work. The amount and quality of such work required for success in these researches are such that they form a striking testimony to his industry and enthusiasm, as well as to his manipulative and experimental skill. In the course of this work he experimented in almost every conceivable way, with spherical and pear-shaped tubes and tubes with necks (something like a sealed-off flask) and tubes with electrodes of different shapes and in various positions. One thing that rather puzzled him was this. He found that some concentration of the phosphorescent response could be obtained with convex cathodes if they were mounted so as to intrude a short distance into the necks of necked tubes, the degree of concentration depending on the degree of vacuum. This focusing effect is probably due to electric charges developing on the walls of the neck near the convex cathode. With the convex cathodes mounted so as to project well beyond the opening of the neck and so as to reach nearly to the centre of the spherical part of the envelope a distribution of phosphorescence fairly uniform over the spherical glass wall was obtained.

Much to his regret the writer never discussed with Jackson the further interesting developments of these researches. As there are some matters of considerable historical importance involved he will take the liberty of quoting the words of one who has often discussed them with Jackson and is therefore in a position to express an authoritative opinion. In an account appearing in the *Obituary Notices of Fellows of the Royal Society* (January 1938) Dr H. Moore writes: "To detect any ultra-violet radiation which, originating at the cathode, might be transmitted through the glass walls of the tube, he used screens of phosphorescent materials held close to the tube and in some cases observed that the screens glowed visibly.

"His interest throughout this work was in the phosphorescent effects rather than in the mechanism by which they were produced. His views regarding that mechanism, stated many years later in conversation, were that the electric discharge caused the cathode to emit ultra-violet radiation which, falling on the anticathode, excited the phosphorescent response on the anticathode material. The glow of phosphorescent material held outside the tube was considered to be a secondary phosphorescence excited by ultra-violet radiations present in the primary phosphorescent emission from the anticathode. The fact that radiations emitted by the anticathode could penetrate the glass walls of the tube, and could excite a screen held outside the tube, was taken to indicate that the wave-length of the radiation emitted by the anticathode was not shorter than 3000 Å.

"There can be no doubt that the response of the phosphorescent screens held close to the tube was, in some cases at any rate, due to X rays emitted by the

anticathode and that, had the observations been viewed from a different standpoint, Röntgen's discovery might have been considerably anticipated. At no time, however, did Sir Herbert Jackson advance any claim to be the original discoverer of X rays, or countenance any suggestion that such a claim might be made on his behalf. Throughout these investigations he had considered that he was dealing with comparatively long-wave ultra-violet radiations and he expressly stated on several occasions that the characteristic penetrating power of the radiations emitted by the anticathode was neither discovered nor suspected by him."

In a paper read on 5 March 1896⁽¹⁾ Jackson described a discharge tube, fitted with a concave aluminium cathode and an inclined platinum anode, which he had made and used during January 1894, and with which, or with a replica of which, he had been able to reproduce all the effects described in Röntgen's original announcement in December 1895. This tube, the original Jackson "focus-tube", was used in May 1896 for a demonstration of X rays at a *Conversazione* held by the Royal Society. A very characteristic action at this demonstration was that at one stage Jackson held up his shoe and showed the onlookers the metal nails in the soles projected on the phosphorescent screen. The main features of this tube were adopted universally for the construction of all gas X-ray tubes.

Jackson gave a discourse on phosphorescence at the meeting of the British Association at Bristol in 1898, and a series of juvenile lectures on it at the Royal Society of Arts in 1900. A published account of some of his work on phosphorescence is to be found in *Nature*, vol. 58, p. 559, and the B.A. Reports for the Bristol Meeting, 1898. The account in *Nature* contains many interesting and important statements; among them, that he had prepared specimens of lime which could not be distinguished from pure lime by chemical analysis, but gave rise to red, orange-red, orange, green and blue phosphorescence respectively.

Between about 1900 and 1914 Jackson devoted himself mainly to problems in pure and applied chemistry. Most of this work is unpublished. What is known about it may be found by consulting the notice by H. Moore in the *Obituary Notices of Fellows of the Royal Society* and another, by Richard B. Pilcher, in *The Analyst* for February 1937.

Among his more miscellaneous activities between 1890 and 1914 are the following. He undertook an elaborate investigation of the weathering of stones in Canterbury Cathedral, Westminster Abbey and other buildings, and did a considerable amount of experimenting on methods of treating stones so as to avoid or diminish damage to stones by weathering. He also became interested in the scientific problems presented by laundry work and investigated the action of alkalis, chemical solvents, oils and soaps on different materials and also their detergent action for cleaning materials soiled in various ways. As a result of the information thus obtained he arranged a course of lectures and practical work on the subject at King's College. This was well attended by launderers from a large area, and the practical value of the work and of the advice which Jackson gave in answer to questions raised by those attending the course were much appreciated. In fact, the importance of the step he took when he put his chemical and physical

knowledge at the service of the laundry industry in this very effective manner has been increasingly recognized by those engaged in it. An account of his work on detergents and bleaching agents was given in two series of Cantor Lectures to the Royal Society of Arts in 1907.

Before this he had been investigating the growth of plants in atmospheres free from carbon dioxide but containing various proportions, from 1 to 70 per cent, of carbon monoxide. He found that green plants could grow in such atmospheres and that starch was formed in them during their growth. This work was continued later, in collaboration with Professor Bottomley⁽²⁾.

In 1906 we find him working, in collaboration with D. Northall-Laurie, on the behaviour of acetylene and of vapours of methyl alcohol and acetaldehyde with electric discharges of high frequency. Accounts of these were published by the Chemical Society. In 1906 also he gave a course of juvenile lectures on combustion and flame at the Royal Society of Arts.

Among the very numerous subjects which he studied and experimented on were methods of promoting crystallization of solids by heating in the presence of various salts, the dispersion of clays in colloidal suspension, the production and testing of refractories, chemical reactions between solids at high temperatures, physical changes in solids at high temperatures, pottery and porcelain, glasses, and problems arising in the manufacture of gun-cotton. As a result of his work on this last subject he made suggestions for modifications in the processes of manufacture with the object of retarding such deterioration of the product as might lead to its spontaneous combustion when in store.

One striking characteristic of Jackson was his interest in and affection for any instrument or apparatus which was useful for chemical researches or chemistry in any sense. In this category we may perhaps classify his interest in photography. Before dry-plate photography was developed he was experimenting on the preparation and sensitizing of emulsions and on methods of developing plates coated with the different experimental emulsions thus obtained. Afterwards he investigated the suitability of many reducing agents for use as photographic developers, and produced special developers both for ordinary plates and for plates for colour photography. He also developed a variety of novel toning baths for photographic prints. Jackson was a keen and accomplished amateur photographer and had a fine collection of stereoscopic photographs, colour photographs, prints and lantern slides which he had made. On the scientific side he experimented in almost every chemical process involved in photographic technique.

In the use of the microscope Jackson was a master. Familiar with all the usual microscope objects, adept in microscopic manipulation and technique, and having a thorough understanding of the microscope as an instrument, he contrived to make use of it in almost all his work. The numerous purposes to which he applied it included the examination of his chemical preparations and the investigation of the effects of heat and various physical and chemical treatments on clays, fibres, porcelains and other materials, objects and substances. He was intimately acquainted with the appearance of a vast number of subjects when viewed with the microscope

and under different methods of illumination as well as with the diffraction effects presented by various small objects when illuminated in different ways. As a result of this wealth of knowledge and his manipulative skill and dexterity, combined with his insight into chemistry and physics, he was often able to tell more in a few minutes about the nature of a given specimen and what had happened to it than others using the same or different methods could in as many days. He was always ready to put his experience of the microscope at the service of others by way either of advice or of the actual examination of specimens. In fact, it obviously afforded him great pleasure to be allowed to do so in any worthy cause.

Another optical instrument in the use of which Jackson was an expert was the spectroscope. He employed this for the detection of traces of inorganic bodies present as impurities or as colouring agents in drugs, glasses, metals, salts and other substances, or introduced into fabrics, leathers, papers and other materials during manufacture.

At the beginning of the Great War Jackson's advice was sought about a number of problems, including the manufacture of toluene and of certain drugs, and about work connected with the Censor's Office. He also served on many of the committees dealing with the production and supply of essential war materials.

At this period the country was faced with serious difficulties owing to the shortage, and in some cases impending exhaustion, of supplies of a number of special kinds of glass, the majority of which had previously been obtained from abroad and mainly from Germany and Austria. The precise composition and the method of manufacture of most of these glasses were unknown. The task of remedying this situation was entrusted to Jackson shortly after the outbreak of war by the Research Committee of the Institute of Chemistry. This was a matter after Jackson's own heart, and in the prosecution of it he was indefatigable. What he accomplished can only be described as amazing. In a very few months he had developed batch mixtures for about ten kinds of glass, including ordinary soda glasses for laboratory glassware and X-ray tubes, combustion-tube glass, a chemically inactive glass for ampoules, miners'-lamp glass, and other special glasses. The formulae for these were published in the *Journal of the Institute of Chemistry* in April 1915. Sir James Dobbie, at that time President of the Institute of Chemistry, gave Jackson the full credit for these remarkable achievements.

After accomplishing this he worked for the Ministry of Munitions until the end of the war on problems involved in the production and manufacture of glasses and glazes. He developed formulae for a great variety of optical glasses, and also worked out batch mixtures for thermometer glasses, opal backings for thermometers, glasses for artificial eyes, vitrite for the capping of electric lamps, a special heat-resisting glass similar in composition and properties to the Pyrex glass which was produced commercially, though not by him, several years later, and other special glasses. A glass similar to his miners'-lamp glass was immediately adopted for cooking utensils. In March 1916 the President of the Board of Trade expressed the Board's appreciation of the services rendered by Professor Jackson to the glass industry. Much, perhaps most, of this work on glasses was done at night in a small laboratory

which he had fitted up at the top of his house at 49 Lansdowne Road, Holland Park, W. In fact, Jackson worked most of the night as well as all day at this period. The pace would have damaged permanently a man of less robust constitution. It is known from the specimens and records which he kept that the number of experimental melts which he made was considerably over 500, and he developed successful formulae for the production of over 70 kinds of glasses. All through this period he was continually consulted by glass manufacturers and engaged in frequent visits to glassworks all over the country helping to overcome difficulties, which inevitably cropped up in the initial stages of large-scale production. It would be difficult to overestimate the value and importance of his work on the production of glass during this critical period. In recognition of this and of his other war-time services he was created Knight Commander of the Order of the British Empire in 1917. He was also elected a Fellow of the Royal Society in the same year.

In 1918 he accepted the invitation of the Council of the British Scientific Instrument Research Association, created in that year as part of the Research Association Scheme of the Department of Scientific and Industrial Research, to become its first Director of Research. Among the numerous qualities which ensured his success in this capacity were his knowledge of, familiarity with, and affection for a wide range of instruments, his great experimental skill in a variety of directions, possibly unequalled, his insight into what could not be done and what could and with how much and how little difficulty. Other important qualifications were his knowledge of the optical and glass industries and acquaintance with their personnel, his quick mind and rapid grasp of a problem and his sure instinct to get down to the roots of it, his remarkable memory combined with the vast extent and extreme variety of his experimental experience and his thoroughly practical outlook and, possibly the most important single factor, his genial personality. After his retirement from the position of Director of Research of the British Scientific Instrument Research Association in 1933, he was a member of its Research Committee up to the time of his death.

In 1919 he delivered the Sir Henry Trueman-Wood Lecture at the Royal Society of Arts on "Glass and some of its problems",⁽³⁾ and in March 1927 he gave a discourse at the Royal Institution on "Some colouring agents in glasses and glazes".

Jackson was keenly interested in ancient glass and ceramics, particularly Chinese ware. His extensive knowledge of the behaviour of clays and of mixtures of clays and other substances, together with his great skill with the microscope, often enabled him to ascertain the manner in which such objects had been fired and to imitate them. His knowledge of glasses and glazes and of the different colour effects caused by the admixture of different chemicals with glasses of various types enabled him to identify the nature of glazes and the substances used to produce particular colour effects in glasses. In this way he was able to provide archaeologists and connoisseurs with valuable information which up to then had been unknown. One of his striking successes in this field was the discovery of the nature and composition of a scarlet glass of ancient Egyptian origin, which he also successfully reproduced.

Sir Herbert Jackson must have been one of the most versatile men of his time. He could talk with vivacity, interest, knowledge, fluency and conviction about almost every conceivable subject. The way in which he was generally regarded as having universal knowledge and experience may be illustrated by the following true story. Some men were discussing the question of the weight of a horse, a subject on which they were not well informed, when one of them said: "Here comes Jackson. He knows everything. Let's ask him." When Jackson started his reply with the words: "When I last weighed a horse——" they all burst into laughter. That Jackson would have some reliable information about the weights of horses they had taken for granted, but that it should be of so direct and first hand a nature as his words implied seemed incredible. The writer, however, has little doubt that Jackson had weighed a horse and on more than one occasion.

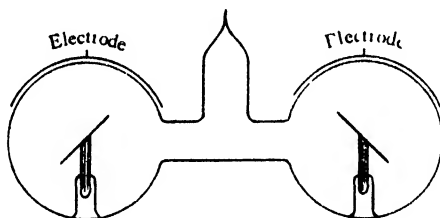
Jackson was a Fellow of the Institute of Chemistry, an institution in connexion with which he was very active, as Examiner, over periods totalling 8 years, as a Member of Council from 1904 to 1907, as a Vice-President from 1907 to 1908, 1916 to 1918 and 1921 to 1924, as a Censor from 1918 to 1935 and as President from 1918 to 1921. He was a Fellow of the Chemical Society and, for a period, a member of its Council.

To the various honours, dignities, public offices and positions otherwise important he received or occupied, which have already been mentioned in this notice, the following list may be added. He was a Fellow of the Physical Society (elected 1916), a Fellow of the Institute of Physics, an Honorary Fellow of the Royal Microscopical Society, an Honorary Member of the British Institute of Radiology, the President of the Röntgen Society from 1901 to 1903, a Vice-President and Member of Council of the Royal Society of Arts, a member of the Interdepartmental Scientific and Technical Committee on Optical Glass, and Chairman or a member of several committees connected with the Department of Scientific and Industrial Research, including the Adhesives Committee, the Stone Preservation Committee and the Building Research Advisory Committee. He was a member of the Advisory Committee on Scientific Research of the London, Midland and Scottish Railway and of other Committees of similar importance. He was a Member of the Senate of the University of London for a period of some years, a Governor of the Imperial College of Science and Technology, and the Chairman of the Technical Optics Committee of the Imperial College. He became a Member of the Royal Institution in 1924 and was a Manager of the Institution from 1930 to 1932 and from 1934 to 1935. He was elected a member of the Athenaeum in 1914 and took an active interest in the club and its affairs throughout the rest of his life.

Although he was a master of so many different branches of knowledge Jackson was by profession a chemist. As an illustration of the effect of his contact with his professional brethren and of some other matters the writer wishes to quote a passage from a notice in *The Analyst*, already referred to. It was written by one of his early students at King's College, R. B. Pilcher, Registrar and Secretary of the Institute of Chemistry, who is more familiar than the writer with this side of his activities. The passage is as follows: "If he did not achieve the reputation of a distinguished

chemist so soon as he deserved it was due to his dislike of putting pen to paper, although he was ever ready to impart his findings to his colleagues and students. Indeed, fellow chemists and others were often indebted to his inventive genius for original ideas, in the solution of problems and in devising chemical and physical apparatus, for which he received no material advantage and little or no credit. . . . Those who have worked with him have remarked that, at times, he seemed to possess imagination or intuition which enabled him to foretell results with almost uncanny accuracy. Indeed, when a research worker suggested a problem he would very likely be informed by Professor Jackson that he himself had already worked on it and had obtained certain results. This was a little disconcerting, perhaps, and it was sometimes thought that he had deceived himself, or was merely surmising, but he was invariably right as to the results."

In the early days of X rays Jackson constructed and experimented with X-ray tubes of almost every conceivable kind. He made one with external electrodes that worked. The construction and mode of operation of this tube will be clearer by reference to the figure. The glass envelope consisted of two spheres about 5 cm. in diameter joined by a straight tube about 4 cm. long and about 1 cm. wide or a little more, so as to form a symmetrical structure like a dumb-bell. The external electrodes were spherical metal caps of thin sheet extending to about a third of a hemisphere, and of the same curvature as the outer surface of the glass sphere to



which they were applied. The straight connecting tube had a side tube joining it at right angles in the middle, the whole forming a T-piece. This was initially connected to the pumps and afterwards sealed off. The external electrodes fitted the spheres and were applied as shown in the figure. The anticathodes thus generated X rays in cones having their axes either close to or roughly parallel to the axis of the connecting tube, and the whole structure was symmetrical about a plane perpendicular to this axis and containing the axis of the side tube. This tube gave X rays when the internal pressure was comparatively high, and the sharpness and symmetry of the focus depended on the centering and sphericity of the bulb, or of the part covered by the external electrodes. The X rays came from the target opposite to the electrode which was connected to the positive side of the induction coil.

The writer of the notice is indebted to Dr H. Moore for the following account of the way in which this very unusual X-ray tube probably functions. As the external electrodes become charged, the positive ions in the gas inside the tube are attracted to, and collect on, the inner surface of the glass beneath the negatively charged

electrode, while the negative ions and any electrons are attracted to the inner surface of the glass beneath the positive electrode. As soon as the surge from the induction coil is over, the external electrodes lose their respective charges, since they are connected to the secondary terminals of the induction coil, and are either completely discharged, or may become weakly charged, possibly in the reverse direction owing to the discharge through the induction coil being of an oscillatory character. The charges on the inner surfaces of the glass beneath the electrodes will then find themselves in an unstable condition, and will begin to disperse. From the negatively charged surface, the first units to escape will be the negative electrons, and they will escape while there is a strong accelerating field due to the negative ions distributed over, or still within a very small distance of the surface. The electrons will thus acquire comparatively high velocities immediately after the positively charged external electrode becomes discharged and, in striking the centrally mounted target, will emit X rays of appreciable penetrating power. The pressure in this tube was much higher than that of an ordinary X-ray vacuum, so high that in an ordinary discharge tube the electrons would have been caught by positive ions or gas molecules before they had travelled across to the target. It is probable that their traversing this path without being stopped is due to the facts that they would not be deflected very much by neutral molecules owing to their high speeds and also that there would be very few positive ions left in that part of the tube.

Jackson's famous focusing X-ray tube was a revolutionary improvement on all its predecessors. All of them gave beams of X rays coming from large and for the most part ill-defined and badly controlled areas. None of them could produce anything which could reasonably be called a picture. Jackson refused to patent his invention, a denial which should be remembered with gratitude by the public. It is said that had he done so he would have had a master patent covering all subsequent X-ray tubes. This is a matter of opinion or conjecture; but it is a fact of history that, although Jackson published his focusing X-ray tube in 1896 and demonstrated its capabilities at a Royal Society *Conversazione* in the same year, it was not until 1913, when Coolidge's thermionic cathode tube made its appearance, that any subsequent improvement, possessing both useful and practical importance as well as novelty, in the art of constructing X-ray tubes occurred. It is possible to regard Wehnelt's X-ray tube with a hot lime cathode (about 1905) as an anticipation of Coolidge's invention. It is probably as close an anticipation as could have been constructed and made to work with the materials available at the time; but it does not seem to have been of much use as a commercial or practical X-ray tube.

Whatever Jackson may or may not have done, he was the first to obtain an approximately point source of X rays and the first to construct an apparatus which produced anything which could now reasonably be called an X-ray picture, and he was the first human being to observe such a picture. Moreover, he did all this within a few weeks or at most a few months of Röntgen's announcement of his discovery. This accomplishment was no accident. It was the result of Jackson's particular and unusual combination of talents. These included a profound physical and practical insight into optics, unrivalled skill in the arts of constructing and

experimenting with vacuum electric discharge tubes and a wide and practical knowledge of phosphorescence and of phosphorescent substances and materials, together with a mastery of the photographic arts, all these being combined with great energy and unbounded enthusiasm for experimenting.

In 1900 he married Amy, the eldest daughter of the late Mr James Collister, a lady of great charm who survives him. Herbert Jackson was a glowing personality, a fine friend and a delightful companion. He was generous to a fault, both with gifts and hospitality, and also in helping those who worked with him, or under him, or who were associated with him as colleagues, as well as those who came to consult him about the many matters of which he was a master or on which he was a recognized authority. He was a man of happy disposition, kind-hearted and public-spirited. He will long be gratefully remembered by a wide circle of friends, former colleagues and old students and, indeed, by a host of people of all sorts with whom his very varied activities brought him into contact.

O. W. RICHARDSON.

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THE VARIATION OF VOLTAGE-DISTRIBUTION AND OF ELECTRON TRANSIT TIME IN THE SPACE-CHARGE- LIMITED PLANAR DIODE

BY R. COCKBURN, M.Sc., A.INST.P, West Ham Municipal College

Proc. Phys. Soc. 50, 298 (1938).

DISCUSSION

MR W. E. BENHAM. The author's analysis supplies in a most desirable form the static basis on which dynamic investigations of valve action must depend. As he indicates in his opening paragraph, the static transit time is of paramount importance. I would add that, even when the signal voltage is large, a knowledge of the static transit time is still required. Conversely, however small the signal, variations in electron transit time from the static value are of importance. There is a close connexion between the variation time and the electron convection current, and this connexion is particularly valuable in the temperature-limited condition (see, for example, reference 2 of the paper). The large percentage of time occupied by outgoing electrons between cathode and potential-minimum is likely to lead to complications when alternating voltages of high frequency are present. At low frequencies, where variations from the static transit time are of less importance, alternating current is derived only from a small range of initial velocities. Thus,

consider a triode with one volt alternating at the grid plane; let the height of the potential-minimum change by 5 millivolts between peaks as a result. Then, if V_0 represents the energy in electron-volts which an electron must have at the cathode in order to succeed in just passing the minimum with no signal,

$$(V_0 - 2.5 \cdot 10^{-3}) - (V_0 + 2.5 \cdot 10^{-3})$$

represents the range of initial velocities which, at very low frequencies, alone contribute to alternating anode current. The electrons which are of velocity greater than $(V_0 + 0.0025)$ will pass whether there is alternating voltage or no, and are thus, except at high frequencies, no better than saturation current in a temperature-limited condition. It is sound to design sensitive valves to work under conditions for which V_0 is the most probable emission velocity, though in coated-cathode valves this would tend to be prejudicial to life.

I would take this opportunity of mentioning that the analysis of § 4.4, reference 10 of the paper, now appears to me to be inapplicable to the case worked out on pp. 24 and 25, so that equation (91) and parts of tables 1 and 4 are wrong.

In regard to applications it may be mentioned that in high-frequency screened-grid and pentode valves the input and output impedances depend, inter alia, on a knowledge of electron transit times in the various spaces concerned. As an application of rather wider scope may be mentioned the fact that if electron essential effects are correctly included, the dispersion of electromagnetic waves can be explained without recourse to frictional terms.

MR D. M. TOMBS. The theory as outlined in the paper calls for as much as 25 per cent increase in transit time due to traverse from cathode to potential-minimum. J. Müller, in experiments on planar diodes, showed a close agreement between his results and his theory in which no allowance was made for transit from cathode to potential-minimum. Has the author been able to compare his results in this connexion with Müller's, or to make experiments himself?

AUTHOR'S REPLY. In reply to Mr Tombs: While it is true that the transit time between cathode and potential-minimum can be quite a large fraction of the total cathode-anode transit time, it does not follow that the total transit time is increased by this amount, since there is at the same time a reduction in the transit time between potential-minimum and anode. Thus, as is shown in figure 6, the total transit time may not be greatly different from the value for zero initial velocity used by Müller (*Hochfrequenztech. u. Electroakust.* **43**, 6, 195).

In considering Müller's results it should be noted that no allowance has been made either for initial velocities or for the large variation of transit time which can occur as the diode becomes space-charge saturated.

I have not yet had an opportunity of verifying his results experimentally with a plane diode.

REVIEWS OF BOOKS

Thermodynamics, by E. FERMI. Pp. x+160. (London: Blackie & Son.) 12s. 6d.

Each generation of teachers no doubt tries to avoid the errors of its immediate fore-runners, which of course it feels well qualified to judge since it suffered from them itself. We have just passed through a period when formal instruction in thermodynamics was reduced to a minimum, and a sign that we have entered the next phase is the rapid increase in the number of text-books on the market. This one does not fall below the standard that we should expect from its author, and those who have heard him speak either English or German will not be surprised to learn that it is written with a better sense of style than several which have recently appeared.

The scope is roughly that of other physics texts on thermodynamics; not that of engineering texts nor that of physical chemistry books, nor yet that of the books written for the out-and-out mathematician. It opens with chapters on the first and second laws (which are not treated in so much detail, either philosophically or historically, as in some other recent books) and proceeds to entropy and the thermodynamic potentials. Further chapters deal with gaseous reactions and dilute solutions respectively, and as an indication that they do not wander afield, we may note that neither "activity" nor "fugacity" occurs in the index. The last chapter, which deals with Nernst's theorem and the entropy constant, shows Fermi's originality more distinctly than the earlier ones.

Whilst the book is mainly concerned with fundamentals, it does not overlook the need for practice in details, and exercises are appended to each chapter; one of those from the final chapter may serve to indicate both the scope of the work and the standard of student for whom it is intended. Problem: "Calculate the degree of dissociation of sodium vapour at a temperature of 4000° K. and a pressure of 1 cm. of mercury. (Take into account not only the pressure due to the sodium atoms, but also the contribution of the ions and the electrons.)"

J. H. A.

The Fundamental Principles of Quantum Mechanics, by E. C. KEMBLE. Pp. xviii+611. (McGraw-Hill Publishing Co., Ltd.) 36s. net.

This volume is a recent addition to the International Series on Physics. The form and appearance of these publications are so familiar to physicists that it is only necessary to state that this particular book contains 600 pages in order to indicate its size and comprehensive character. Its purpose and scope will be realized from the author's remark in the preface, that he has been influenced by the desire to meet the needs of graduate students of physics. A chapter has been included on the mathematical background of the theory in order to make the work to some extent self-contained. To give a complete idea of the contents it would be necessary to make a list of the headings of the chapters which are in many cases without any very obvious connexion with one another, so that the book is of the nature of a series of sections on the quantum theory. It is one of the most comprehensive works of reference on the subject and there appears to be no work except Frenkel's *Wave Mechanics* of a similar character.

There are chapters on Schroedinger's theory, on operator and matrix theory, on perturbations and on statistics, to choose only a few. Perhaps the outstanding feature of the work is the care in presentation of the subject which has resulted from the author's desire to be accurate. He has made the attempt to provide a bridge between the difficulties of the exact mathematical technique and the inaccuracies of some of the easy presentations of the subject. The author has without doubt a fine aesthetic physical and mathematical

sense, but, alas, he has not allowed this side of his character full play in the choice of notation. One is put off in glancing through the pages by the symbols with arrays of suffixes, crosses and stars that look like disfigurements. Is there any real need to speak of an operator $T^{(2)}$ or the unit operator $\alpha^{(2)}$? Shorthand can be carried too far, and it is continually necessary to turn back in the search for the meaning of the symbols, and to make matters worse in one place an operator is represented by two symbols.

The author claims to have added new material or to have made a departure in almost every chapter. But one wonders if this is an advantage. Its effect in the present case is to give the impression that he feared he might leave something out. He is not the only writer on quantum theory who seems to err in this respect.

The new quantum theory has now had a life equal to that of the Bohr theory, if we assign to the latter the years 1913-25, and we ought to begin to decide on an accepted mode of presentation combined with an accepted notation. With regard to the latter question we may remind ourselves that very little in the way of new notation has been required in the quantum theory. Mathematicians with true altruism discovered most of the notation necessary, never caring whether it would be useful to physicists or not. Their work might well be copied. It is still difficult to decide on a uniform mode of presentation of the subject because the theory is still growing, though the fundamentals are now largely established. Perhaps the difficulty arises from the attempt to write a book on quantum mechanics; one might almost equally well write on classical physics, so wide has the subject become.

Some of these remarks are not a criticism of the work under review in particular, they have their origin in the numerous publications that continually appear on modern physics and which it is difficult to read because of the variety of notations. There is no doubt that the present volume on account of its careful, complete and exact presentation of the subject is rightly described as a standard work.

H. T. F.

Elementary Physical Chemistry, by HUGH S. TAYLOR and H. AUSTIN TAYLOR.
Pp. xiii + 664. (Macmillan & Co.) 16s.

The first edition of this book appeared 10 years ago; since that time much work has been carried out on problems of atomic and molecular structure and their bearing upon the general field of reaction kinetics. The authors in their discussion of the gaseous state of aggregation introduce the concepts of collision-frequency and of varying velocity of gas molecules, and for this procedure there is a very good reason. In chemical reactions these are factors of prime importance. The study of velocity in gas reactions and the concepts of activation by collision and of gas reactions occurring at surfaces follow. These lead on to a discussion of the second law of energetics and the problem of equilibrium. The authors are to be congratulated on their clear exposition of these aspects of physical chemistry. The classical field of physical chemistry, that of electrolytes, is sub-divided under the headings of weak and strong electrolytes, and an introduction to the thermodynamic treatment of solutions is given. The physicist will study with interest the section devoted to methods for the determination of the charge on the electron, which includes a reference to the work of Birge and McMillan published in 1935 but omits work subsequent to that paper but published in 1935 and 1936. Lawrence's cyclotron is described. Of borderline subjects we are given an account of the work on Langmuir and others on the orientation of molecules, leading on to the more recent work of Rideal on chemical reactions occurring in monolayers. Specialists will inevitably find some omissions when an attempt is made to cover so wide a field: for example, no reference appears as to Kneser's work on the time of relaxation of molecules in collision. In this discussion of the atomic heats of metals the authors' brief account tends to give the impression that the Debye

formula fits the results with accuracy. Actually it does not do so, as was shown by Griffiths in the *Philosophical Transactions*, 1914.

The volume will be of great service to both physicists and chemists and the authors are to be congratulated on carrying through a valuable piece of work. E. G.

Trigonometry, by T. M. MACROBERT and W. ARTHUR. Part III. *Advanced Trigonometry*. Pp. xi + 134. 4s. 6d. Part IV, *Spherical Trigonometry*. Pp. x + 61. 3s. (London: Methuen & Co.)

An earlier part of this new trigonometry has already been reviewed in these *Proceedings*, and as regards part III, it only remains to add that it follows directly on from the earlier volumes. It deals with the properties of sequences and series, somewhat on the lines of the treatment given in the senior author's *Complex Variable*.

Part IV, one of the few books in English on spherical trigonometry, will be bought by many readers who are not interested in the other parts. It deals only with the fundamentals: the properties of spherical triangles and their polars, the circumcircle and the incircle on a spherical surface, and the solution of spherical triangles. Two whole sections are devoted to the numerical solution of spherical triangles, the work being arranged for the use of logarithms, and to the reviewer it seems regrettable that the haversine method is ignored. This method, used by navigators (where speed is important) and in the Nautical Almanac Office (where accuracy takes precedence of other things) would not be worth teaching to the ordinary student if it required special apparatus or tables. But the formulae are particularly easy to remember, and tables of haversines and log haversines are easily available in Inman's nautical tables or Hall's four-figure tables (Cambridge). For those who are not familiar with it, we may say that

$$\text{hav } A [= \text{half versine } A] = \frac{1}{2} (1 - \cos A) = \sin^2 \frac{1}{2} A,$$

so that $\log \text{hav } A = 2 \log \sin (\frac{1}{2} A)$. Apart from this criticism, which in any case is a matter of opinion, the book is thorough and helpful, and is to be warmly recommended. J. H. A.

Annual Tables of Constants and Numerical Data. Index to Volumes VI to X (Years 1923 to 1930). Pp. xxiv + 352. (Paris: Hermann et Cie, 1937.)

This index is similar in conception to the earlier one, covering volumes I to V. It consists of two parts, the first an alphabetical index to properties and materials with common names. This part is in French, but the English, Italian and German names are entered in alphabetical position, with cross-references to the French names, when necessary. The second and longer part is a classification of compounds according to their formulae. Under each formula are given the properties for which values occur, together with the volume number and page. It will facilitate enormously the task of ascertaining whether data on a given compound are available in the volumes to which it refers.

J. H. A.

Tables Annuelles Internationales de Constantes. Vol. XI, 1st Part. Pp. xxii + 493. (Paris: Hermann et Cie, 1937.)

Several times in the history of the Annual Tables a serious lag has grown up between the date of publication and the date of recording of data. At the moment, all data subsequent to 1930 require collection. The data up to 1936 will be included in two volumes, nos. XI and XII, each of which will be divided into three parts, though the six parts will only make four books, viz. vol. XI, part 1; vol. XII, part 1; vols. XI and XII, part 2; and vols. XI and XII, part 3. In addition, two sections of vol. XI appear only as monographs.

The part before us is part I of the eleventh volume, and covers the years 1931 to 1934. It is printed on a smaller page than that used for previous volumes and on better paper, so that it is now very pleasant to handle and to read. Its first 350 pages are mainly occupied with general physics and heat (acoustics is included, with seven pages) followed by electrical conduction, magnetism, and the minor electrical effects. An interesting opening is a section on universal constants, in which e is given as $(4.805 \pm 0.005) \times 10^{-10}$ e.s.u., h as $(6.62 \pm 0.01) \times 10^{-27}$, $1/\alpha$ as 136.8 ± 0.3 and the absolute zero of temperature as $-273.19 \pm 0.03^\circ \text{C}$.

As far as it has been possible to verify, the editors have spread a fine-meshed net widely, and have missed very little. As usual, the main text is in French, generally duplicated in English, whilst the introductory matter is also given in German (where *Dichte* and *Zähigkeit* are interchanged on page vi) and Italian. The subjects for which we must wait until parts 2 and 3 are optics, atomic physics, physical chemistry and metallurgy, though some sections from these have already been completed and have appeared in monograph form. An index to all the parts of volumes XI and XII is promised in due course, similar to the index to volumes VI to X, which receives notice elsewhere in this issue.

J. H. A.

Annual Tables of Constants and Numerical Data

1. *Deuterium*, by G. CHAMPETIER, Mlle BONNET and M. MAGAT. Pp. 78.
9. *Electromotive Forces*, by H. S. HARNED. Oxidation-Reduction Potentials, by G. ÅKERLÖF. Pp. 45.
11. *Molecular Spectra and Molecular Structure*. Part I, by V. HENRI. Pp. 96.
12. *Molecular Spectra and Molecular Structure*. Part II, by V. HENRI. Pp. 66.
13. *Paraday Effect*, by M. SCHÉRER. Magnetic and Electric Birefringence, by A. COTTON and J. RABINOVITCH; Photo-electricity by G. A. BOUTRY. Pp. 40.
14. *Combustion and Detonation of Gases*, By P. LAFITTE. Pp. 28. (Paris: Hermann et Cie, 1937.)

As was announced in the preface of a recent volume of *Tables Annuelles de Données Numériques*, it is intended in future to sell the various sections of each volume separately, though of course the whole volume can still be obtained bound. It will be noticed that, to facilitate this arrangement, the pagination now commences afresh in each of the sections or subsections, the number of which precedes the actual page number. Thus 70-9 is p. 9 of section 70 (which occurs in monograph No. 14). The literature covered by the sections under review is not all of exactly the same period, but it is all quite recent. The sections form useful supplements to any other tables and it is interesting to note that they tend more than in the past to cite references instead of copying out the data, where these are bulky.

To turn over the pages of the monograph on deuterium and its compounds (to take an example almost at random) is an impressive reminder of the rate at which measurements of very varying worth are being added to the world's stock of information, a rate so great that it is not surprising to find voices lifted from time to time urging us to slow down. The rate leads to the need for such tables as these, as well as for various abstracting periodicals; and then requires monographs and annual reports to help us to take stock periodically.

J. H. A.

THE PROCEEDINGS OF THE PHYSICAL SOCIETY

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THE ELASTIC PROPERTIES OF SODIUM WIRES BETWEEN -183° AND 90° C.

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ABSTRACT. The elastic properties of single-crystal wires and of polycrystalline sodium are investigated. The results obtained with single crystals are found to be in good agreement with a theory recently given by Fuchs. The characteristic temperature Θ is calculated from the data obtained with the polycrystalline material. A comparison is made with the authors recent X-ray measurements.

§ 1. INTRODUCTION

THE present paper deals with the elastic properties of sodium wires at various temperatures including a close approach to the melting-point. Certain parts of the work are linked up with the author's recent X-ray investigation of sodium⁽¹⁾, in the course of which some numerical data were obtained for the characteristic temperature Θ . This temperature is closely connected with the elastic constants, as is well known from the Debye theory. It can be obtained independently from experiments on elastic properties and thus affords a check on the X-ray data. The second part of the paper, dealing with the elastic properties of single crystals in different crystallographic directions, is interesting in connexion with a theory recently given by Fuchs⁽²⁾.

A few months after the experiments had been started, two short notes dealing with the elastic constants of sodium at 80° K. appeared in the *Physical Review*⁽³⁾. The first of these furnished evidence of a considerable discrepancy between the experiments and Fuchs's theory. In the second note the authors rectified an error in their calculations and claimed to have found a good agreement between theory and observation; such agreement is found in the present work also. The agreement between the experimental data is particularly satisfactory in view of the differences in the experimental technique. The American authors worked with ultrasonic vibrations, whereas the present measurements were made with comparatively slow oscillations whose frequencies lay between 20 and 200 c./sec.

§ 2. EXPERIMENTAL DETAILS

The torsion modulus. A cylindrical magnet attached to the free end of a vertical sodium rod or wire is set into resonant oscillation by means of a variable speed alternator connected to a pair of Helmholtz coils. The torsion modulus of a polycrystalline rod is given by

$$\frac{8\pi I}{r^4 p^2}$$

... (1),

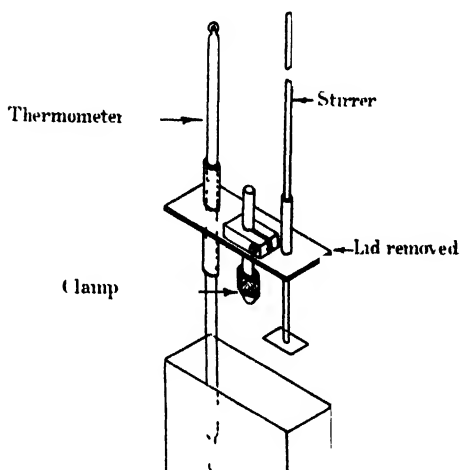


Figure 1.

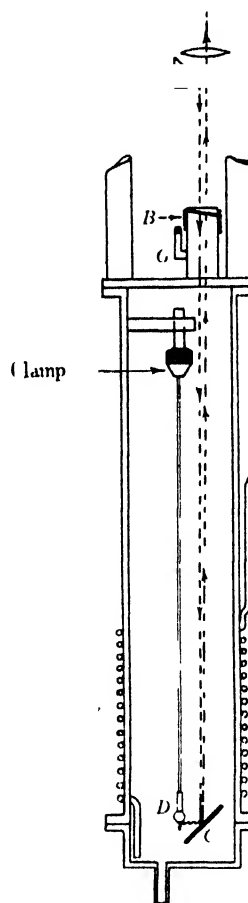


Figure 2.

where I is the moment of inertia of the magnet about the axis of oscillation, l and r are the length and radius of the rod, and p is the resonance period. The correction term due to the moment of inertia of the rod is negligible. Oscillatory current up to 60 c./sec. is obtained by reversing direct current with a commutator, and for frequencies between 30 and 500 c./sec. an alternator giving a sinusoidal output of 10 cycles per revolution is used. The speed of these machines is accurately controlled. The period of the vibrating magnet is deduced from the measured number of revolutions per second.

Measurements from 20 to 90° c. are made with the specimen immersed in oil

in a copper container measuring $22 \times 8 \times 2\frac{1}{2}$ cm. (figure 1). The lid of the container has a stirrer, a thermometer and a serrated four-jawed clamp which holds the upper end of the torsion rod. *A* is a glass window for the beam from the mirror. Purified thin paraffin oil is used, and a correction for its effect on the oscillator is applied. The outside of the container is fitted with flat electrical heaters, not shown on the drawing. For the measurements between 20 and -183° C. the specimen is placed in an atmosphere of an inert gas. The gas-container, figure 2, which fits inside a Dewar flask, is a brass tube whose top end is bolted to a plate *A* and whose lower end contains a mirror *C*, adjustable by means of three screws which can be made to have a gas-tight fit.

The vibrations are made visible with the aid of light reflected from a small mirror at the free end of the oscillator. The light passes through a window *B*, is reflected

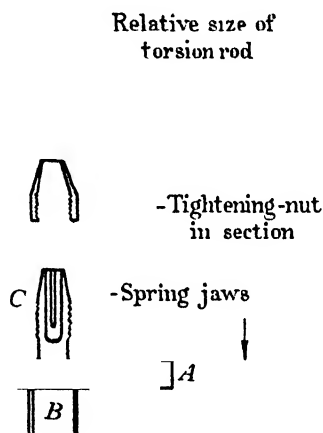


Figure 3.

at *C* on to the mirror of the oscillator *D*, and travels back along its own path. An image $\frac{1}{4}$ mm. wide is formed 80 cm. away by the lens *L*. When necessary a Dewar vessel, sliding in guides and containing either solid carbon dioxide and alcohol or liquid oxygen, is raised from below. To protect the sodium and promote temperature-equilibrium an inert gas, either argon or nitrogen, precooled by a spiral *F*, enters the lower end and leaves the upper end of the vessel by the non-return valve *G*. Oxygen and moisture are removed from the gas by causing the latter to pass first through a vessel containing about 15 ft. of sodium wire, then over 3 ft. of sodium wire in a tube heated to 75° C., and finally through a liquid-air trap.

The sodium specimen is made to vibrate by the action of the alternating field on a steel rod *A* (figure 3). This rod is attached to the free end of the sodium wire by a clamp with two serrated jaws which fit the diameter of the wire. The mirror *B* enables the vibrations to be observed. Five different clamps and rods are used, each having a different moment of inertia (see table 1). Uniform results are obtained so that, in view of column 7, we infer that the longitudinal stress to which

the rod is necessarily subjected does not affect the torsion modulus. The resonance frequency is easily observable at all temperatures.

Table 1

Oscillator	<i>a</i> (cm.)	<i>b</i> (cm.)	Total weight <i>W</i> (g.)	Moment of inertia (g.-cm. ²)	Diameter of torsion rod (cm.)	Stress on torsion rod due to <i>W</i> (g./mm. ²)	Range of periods used (sec.)
No. 1	3.45	0.27	3.3	1.25	0.11	3.5	0.048 to 0.064
No. 2	3.25	0.35	4.1	2.20	0.2	1.3	0.023 to 0.04
No. 3	4.17	0.42	5.78	8.54	0.23	1.4	0.024 to 0.04
No. 4	3.0	0.48	5.1	3.24	0.24	1.1	0.015 to 0.025
No. 5	3.1	0.5	6.1	3.28	0.33	0.72	0.010 to 0.012

The extension modulus. This is found by means of transverse vibrations of the sodium specimen. The apparatus consists of a rectangular gas-container measuring $14 \times 5 \times 2.5$ cm. with one of its sides of glass (figure 4). A beam or rod of sodium

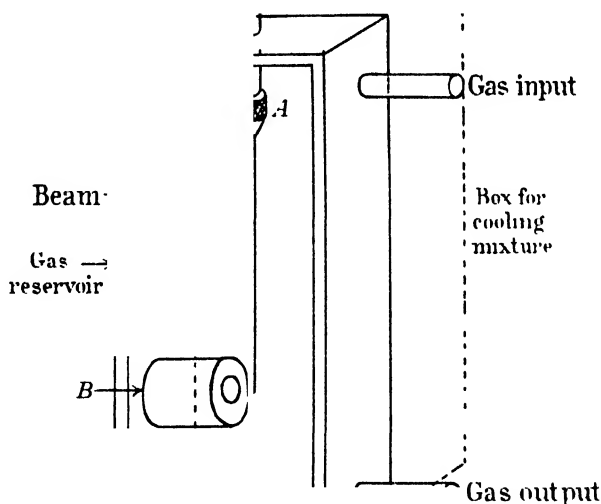


Figure 4.

is held by a clamp *A*. An iron wire 2 mm. long is pushed into the sodium at the free end. Vibrations of the specimen are caused by the intermittent pull exerted on this iron wire by the magnet *B*, and are observed with a microscope. An estimate of the temperature factor is made by surrounding the beam (except at its extreme free end) with a concentric copper tube (not shown) fixed to the copper back of the container. This back forms part of a box, shown dotted, which is filled

with solid carbon dioxide and alcohol. The temperature of the copper tube is measured by a thermocouple. The resonance period of the beam is excited when the period of the alternating current is 2, 4, 6, ... times that of the beam. The extension modulus is given by the well-known expression

$$Y = \frac{4\pi^2 l^3}{3Ip^2} \left(M_0 + \frac{33}{140} M \right) \quad \dots\dots(2),$$

where l is the length of the beam, I its moment of inertia, M its mass, M_0 the weight of the load at the extreme end, and p the resonance period.

Production of sodium rods. The polycrystalline rods are extruded from a sodium press. They vary from 1 to 3.3 mm. in diameter, and appear to be uniform in thickness if prepared with care. Single-crystal rods are formed by sucking molten sodium up a glass tube which is then cooled along its length. When cold the sodium rods can easily be ejected. They usually have a slight taper. The accidental bending of the rod during mounting is nowhere sufficient to give a radius of curvature less than 10 cm. During the process of mounting the oil apparatus is filled with purified paraffin; for the gas-container purified petroleum ether with a boiling-point of 40 to 60° is used, the container being filled with the liquid until the mounting is complete and the apparatus is gas-tight. The petroleum ether is then replaced by the inert gas.

Performance of apparatus. The determination of the torsion modulus requires a knowledge of (a) the moments of inertia of the oscillators, (b) the resonance period, (c) the effective length of the torsion rod, and (d) the radius of the torsion rod. (a) The moments of inertia are calculated and checked by comparing their ratios. (b) The amplitude of the resonance vibration, at 20° C., falls to half its value if the motor-speed is changed by $2\frac{1}{2}$ per cent. At -183° C. the peak is sharper, and a beat is often observed when the motor is just off resonance speed. The specimens continue their vibrations when the external field is switched off. They perform about 10 oscillations at room temperature and about 70 oscillations at -180° C. before the amplitude falls to half its value. The periods of the vibrations of square-topped wave-form, determined by the reversing commutator, and of those of sinusoidal wave-form, determined by the alternator, are the same. The period is independent of the amplitude provided the amplitude does not exceed $\frac{1}{2}^{\circ}$. The effect of the oil is found by comparing the periods of a copper torsion wire in air and in oil. The oil increases the period by 5.4 per cent at 20° C. and by 5.3 per cent at 90° C. The correction is almost independent of the oscillator and of its frequency. (c) With an error not exceeding 1.5 per cent the distance between the clamps may be taken as the length of the rod, if this is greater than 6.5 cm. In general lengths between 11 and 15 cm. are used. For rods shorter than 6.5 cm. the square of the period is no longer proportional to the length, the apparent reason being that in order to produce an observable amplitude the short rods are strained beyond the elastic limit. (d) Except for the smallest wire the values of r^4 as determined by microscope readings and by weighing usually agreed to 1.5 per cent. For the smallest fibre the discrepancy is doubled. The measurements of the

extension modulus are less accurate than those of the torsion modulus. The force maintaining the oscillation is not a push-pull, as in the torsion experiments, but an intermittent pull. The mass of the last 1 mm. of the beam, which contains the iron wire, is considered to be the M_0 in equation (2), and l is the full length less 1 mm. Beams are circular in section and between 1.1 and 3.3 mm. in diameter. The period is constant up to amplitudes of 0.5 mm., the smallest observable being 0.05 mm. An apparent decrease in the modulus occurs for the beams of largest diameter if their lengths are less than 4 cm. Such specimens are probably strained beyond their elastic limit even at small amplitudes. Higher harmonics of vibration are absent and there is no difference between vertical and horizontal beams. A rotation of the beam round its axis does not affect its period.

§ 3. RESULTS AND CONCLUSIONS

Polycrystalline rods; torsion modulus. The experiments show that the torsion modulus often varies by from 5 to 10 per cent. These variations are most probably due to the variation in the microstructure of the rods. It is well known that the individual crystals in polycrystalline sodium are much larger than those found in other metals, as is shown clearly in the typical Laue photograph, figure 5*a*. In a

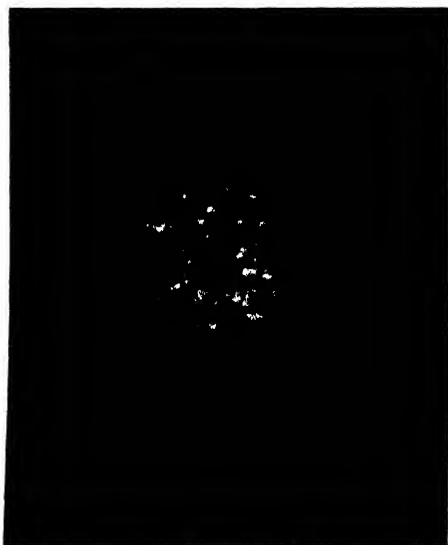


Figure 5*a*.

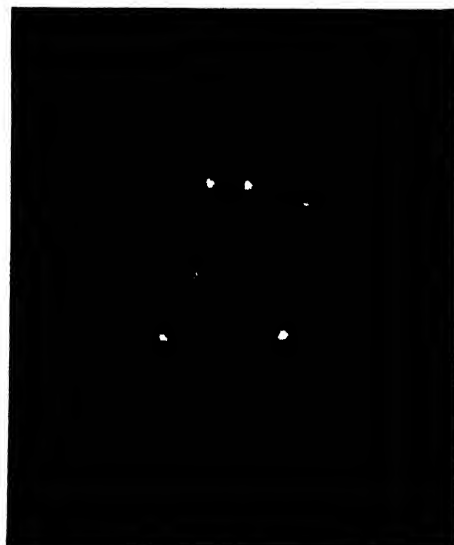


Figure 5*b*.

material consisting of a comparatively small number of individual units oriented at random, the statistical fluctuations are bound to be more pronounced than in a very fine-grained material. The temperature coefficients of the individual rods vary very little. The investigation of the torsion modulus is therefore carried out in the neighbourhood of 20° C. The modulus does not appear to be altered by bending the rods to a radius of 5 cm. and straightening or even giving them a permanent twist of 180°. The maximum error for any one experiment does not

exceed ± 8 per cent for the rods 1.1 mm. in diameter, and is about 6 per cent for the other rods. The data observed at room temperature are given in table 2.

Table 2

Diameter of torsion rod (cm.)	Sample of sodium	Torsion modulus at 20° C. (10^9 dyne/cm ²)
0.115	Commercial	9.0
0.115	"	9.7
0.17	"	8.9
0.17	"	9.9
0.17	"	10.8
0.20	"	9.7
0.20	"	7.8
0.20	"	10.3
0.20	"	9.6
0.20	"	9.4
0.24	"	8.6
0.24	"	10.0
0.24	"	9.7
0.24	"	9.0
0.24	"	9.5
0.24	"	8.9
0.33	Hopkins and Williams commercial	9.6
0.33	"	9.4
0.33	"	9.3
0.24	"	9.7
0.24	"	10.0
0.33	Hopkins and Williams; analytical reagent purity	9.8
0.24	Kahlbaum; analytical reagent purity	9.9
0.24	"	10.8
0.24	"	11.3
		Mean = 9.6

Oxidation of a rod causes a serious error at low temperatures; a 3-per-cent oxidation results in a 13-per-cent increase in the temperature coefficient. The oxidation was estimated by comparing the weight of the rod with that of an unused portion from which it was cut. The final results, for which the oxidation is less than 1 per cent, are given in table 3 and in figure 6. The torsion modulus is nearly a linear function of the temperature. The large value of the temperature coefficient is consistent with the considerable thermal expansion of sodium.

Polycrystalline rods; the extension modulus. The values of this are given in table 4; they vary with the diameter of the rod. The measurements become more consistent as the diameter decreases, but the experiments obviously do not yield an accurate value. Rough measurements from 20 to -70° C. indicate that the temperature coefficient is about 10 per cent greater than that of the torsion modulus. The extension modulus as calculated from the bulk modulus and the torsion modulus of table 2 is 28×10^9 . This value, which is almost independent of the bulk modulus, may be compared with the experimental values in table 4.

Table 3

Temperature (° C.)	Torsional modulus in terms of its value at 20° C.
90	0.81 0.815 0.79 0.805 0.814
- 79	1.23 1.19 1.21
- 183	1.5 1.51 1.48 1.47

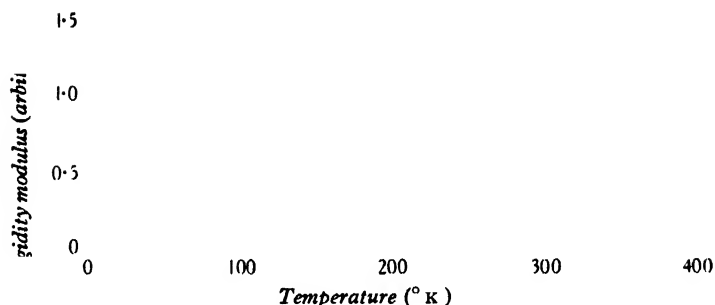


Figure 6.

Table 4

Diameter of beam (mm.)					
2.2		2.0		1.1	
Length (cm.)	Extension modulus (10 ⁹ dyne/cm ²)	Length (cm.)	Extension modulus (10 ⁹ dyne/cm ²)	Length (cm.)	Extension modulus (10 ⁹ dyne/cm ²)
7.1	35	7.1	29.5	4.0	22.5
7.0	35	7.2	22.6	7.0	22.9
3.8	29	3.7	23.6	7.0	23.4
6.0	31	7.2	35.6	7.0	26.0
7.3	41	5.3	36.4	6.6	27.0
6.8	29	4.0	32.2	6.9	29.0
				7.0	29.0
Mean, 33		Mean, 30		Mean, 26	

Polycrystalline rods; the characteristic temperature Θ . The characteristic temperature is calculated in accordance with the theory of Debye⁽⁴⁾. Assuming the validity of the standard relationships between the elastic moduli, the Debye

formula may be transformed into one in terms of the torsion modulus and extension modulus. It is seen that the extension modulus contributes only about 2 per cent of the result, and hence an approximate value for this modulus is sufficient. Θ depends roughly on the square root of the torsion modulus. A close agreement between the values determined from X-ray measurements and from the elastic constants is not to be expected at higher temperatures, but for lower temperatures the agreement is better. The two curves are shown in figure 7. The values extrapolated to absolute zero are reasonably consistent with the theoretical figure given by Fuchs.

Single-crystal rods. The material is examined by the aid of X rays to ensure that the specimen is a single crystal; a typical Laue photograph is shown in figure 5*b*. No great care seems necessary in handling these crystals: a rod deliberately bent to a radius of 5 cm. and straightened had its torsion modulus reduced from 17.0×10^9 to 15.3×10^9 , and the accidental bending is far less than this. The resonance vibrations do not damage the crystals.

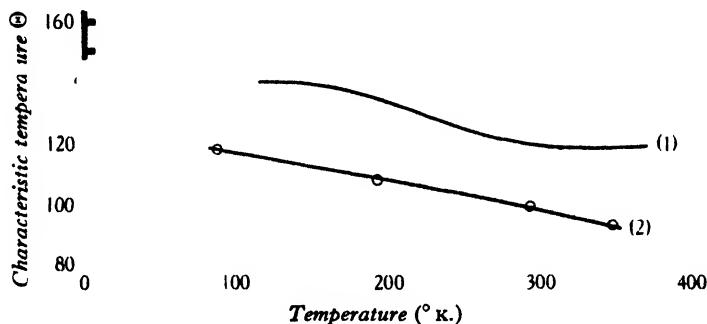


Figure 7. Δ , theoretical point found by Fuchs; (1), author's previous X-ray curve; (2), author's points from elastic constants.

The torsion modulus at 20° C. varies between 9×10^9 and 35×10^9 , while the extension modulus varies between 31×10^9 and 14×10^9 . In table 5 the results are classified in two groups (*a*) and (*b*). In group (*a*) the axis of the rod is parallel to the 100 direction. One of the values is questioned because the rod after being cooled to -79° C., and reheated for 20° C., shows resonance for two speeds of the alternator. These periods give the torsion modulus as 31×10^9 (the original value) and as 22×10^9 . The cause of this double resonance is not understood; it happened only once in about 40 experiments.

The variations of the temperature coefficient as a result of successive cooling and heating amount sometimes to 30 per cent, and are caused chiefly by changes in the torsion modulus at room temperatures. Within 10 per cent no systematic difference is found between single crystals and the polycrystalline material.

In order to compare the theoretical values of Fuchs with the experimental data an extrapolation to absolute zero of temperature is carried out by drawing a straight line through the observed points. The procedure gives probably too high a value for the elastic constants, but the error is not likely to be large considering the small

Table 5A

Displacement of axis of rod from 100 direction (degrees)	Torsion modulus at 20° C. (10 ⁹ dyne/cm ²)	Extension modulus at 20° C. (10 ⁹ dyne/cm ²)
3	35	14.5
10	30 (?)	—
11.5	20	14
17.5	17	—
20.5	17	—
33	12	29

Table 5B

Displacement of axis of rod from 110 direction (degrees)	Torsion modulus at 20° C. (10 ⁹ dyne/cm ²)	Extension modulus at 20° C. (10 ⁹ dyne/cm ²)
Less than 2	9.0	31
10	10.4	—
11	11.5	24.6

range of the extrapolation. The theoretical data given by Fuchs are the constants c_{11} , c_{12} and c_{44} of the elastic potential, in terms of which the torsion and Young's modulus can be expressed. The author is indebted to Dr H. A. Jahn for this calculation which is based on the formulae given by W. Voigt⁽⁵⁾.

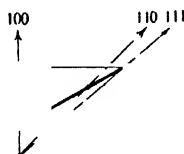


Figure 8.

Table 6

Direction of axis	Young's modulus (10 ⁹ dyne/cm ²)		Torsion modulus (10 ⁹ dyne/cm ²)	
	Theoretical	Experimental (extrapolated to absolute zero)	Theoretical	Experimental (extrapolated to absolute zero)
111	144	—	10	—
110	58	56	—	15
100	20.6	26	58	59

On comparison of the observations with Fuchs's theoretical data there seems to be no doubt that the theory can not only account for the order of magnitude of the elastic constants but also give their correct variation with direction in the anisotropic medium.

§ 4. ACKNOWLEDGEMENTS

The author is glad to express his indebtedness to the Managers of the Royal Institution and to Sir William Bragg for permission to carry out this work. He expresses his thanks to Dr A. Müller for suggesting it and for continuous interest and advice.

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QUIMBY, S. L. and SIEGEL, SIDNEY. *Phys. Rev.* **52**, 665 (1937).
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DISCUSSION

Dr A. MÜLLER. It is to be expected that the elastic properties of a metal are structure-insensitive. Mr Dawton's experimental data are in reasonably good agreement with theoretical predictions, and show that the present-day theory of metal lattices can explain structure-insensitive properties. The situation is quite different when structure-sensitive properties are to be dealt with. The author's previous experiments on the hysteresis effect observed with X-ray reflection from sodium are still unexplained.

Dr R. M. DAVIES. One minor criticism of the paper relates to nomenclature; with the one exception of figure 6, the author consistently uses the term "torsion modulus" instead of the well-established "rigidity modulus". Apart from other considerations, this terminology has the disadvantage of clashing with the usage of engineers, who use the term "torsion modulus" to denote the ratio of the so-called "torsional rigidity" (torque per twist per unit length) to the rigidity modulus.* In the case of a rod of circular cross-section, the rigidity modulus of the engineers is thus $\frac{1}{2}\pi$ (radius)⁴, and, in general, it is a quantity of the fourth power of a linear dimension.

The author's statement that the period of forced torsional vibration was independent of the amplitude "provided that the amplitude does not exceed $\frac{1}{2}^{\circ}$ " is probably connected with the fact that, in the case of the forced vibration of a bar loaded with a magnet and driven by an alternating magnetic field, the period p_a corresponding to maximum amplitude will depend on (i) the magnetic moment of

* R. V. Southwell, *Theory of Elasticity*, p. 323 (Oxford 1936).

the magnet, (ii) the peak value of the driving field.* Alternatively, one may say that p_a will depend on the amplitude of forced vibration of the bar, since the amplitude depends on the magnetic moment and upon the driving field. However, when the amplitude approaches zero, p_a approaches p , the free period, corresponding to zero magnetic moment and zero driving field, and in accurate measurements of Young's modulus and the rigidity modulus by the alternating field method it is necessary to extrapolate the observed p_a s to conditions of vanishingly small amplitudes as shown in the papers quoted above.

Another point which may be mentioned is the restricted validity of equation (2), which is used to calculate Young's modulus from experimental observations. In the notation of equation (2), the general equation for Y in the case of the transverse vibrations of a loaded bar may be written

$$Y = \frac{4\pi^2 M l^3}{I p^2 z^4} \quad \dots\dots(1a),$$

where z is a numeric determined by the ratio M_0/M .

Equation (2), which is Rayleigh's approximation, may be derived from equation (1a) by writing

$$\frac{1}{z^4} = \frac{1}{3} \left(\frac{M_0}{M} + \frac{33}{140} \right) \quad \dots\dots(2a),$$

and this approximation is valid only when $M_0 \gg M$.

In general, the value of the parameter z is given by the transcendental equation†

$$1 + \cosh z \cos z = \frac{M_0 z}{M} (\cosh z \sin z - \sinh z \cos z);$$

an explicit solution of this equation, suitable for numerical calculation, has been given.‡

The data given in the present paper are insufficient to determine the value of the ratio M/M_0 , but it appears that M_0 is comparatively small in comparison with M , and, under these conditions the Rayleigh approximation can be seriously in error. For the purpose of illustration, assume that M_0 is negligible in comparison with M ; equation (2a) gives $\frac{1}{z^4} = \frac{11}{140} = 0.07857$, whereas the true value is $(1/12.36)$, equal to 0.08090; the value is thus 3 per cent in error, and consequently the value of Y calculated from equation (2) will be 3 per cent too small.

Another possible source of error in equation (2) is due to neglect of the effect due to the rotation and shearing of the elements of the bar when in vibration.§ The correction for this effect becomes appreciable only when the length of the bar is not negligible in comparison with its cross-sectional dimensions, and calculation shows that the maximum value of the correction amounts to about $\frac{1}{2}$ per cent in

* R. M. Davies and E. G. James, *Phil. Mag.* 18, 1023 and 1053 (1934); R. M. Davies and I. H. Thomas, *Phil. Mag.* 23, 361 (1937).

† J. Prescott, *Applied Elasticity*, p. 213 (London, 1924).

‡ R. M. Davies, *Phil. Mag.* 22, 892 (1936).

§ R. M. Davies, *Phil. Mag.* 23, 1129 (1937).

the experiments described in the paper. In the present instance, the correction is probably less than the experimental error, but in certain cases it may become important.

Prof. ALLAN FERGUSON said that the constant $\frac{33}{140}$ used in the calculation of Young's modulus assumes that the shape of a cantilever is the same during vibration as during statical deflection. He asked whether the assumption was justifiable in the present case and suggested that the constant $\frac{33}{140}$ might need correction.

AUTHOR's reply. The points raised by Dr Davies do not appear to necessitate any alteration which would affect the results, except for the 3-per-cent correction which may be applied to the values of Y . I must thank him for this, and also for the calculation of the $\frac{1}{2}$ -per-cent error due to the rotation and shearing of the elements of the bar in vibration.

On account of the difficulty in determining the shape of the bent beams I regret that I cannot answer Prof. Ferguson's question.

THERMIONIC EMISSION FROM CARBON

By A. L. REIMANN, PH.D., D.Sc.

Communication from the Research Staff of the M.O. Valve Co. Ltd.,
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Communicated by Dr C. C. Paterson. Received 18 February 1938. Read in title 27 May 1938

ABSTRACT. Observations of the thermionic emission from a carefully outgassed filament of graphitic carbon were made at a series of temperatures between 1665° and 2191° K. The corresponding values of the constants A and ψ in the empirical emission formula

$$i = AT^2 e^{-\psi/kT}$$

were found to be $30 \text{ amp./cm}^2\text{-deg}^2$ and 4.34 eV. respectively.

§ 1. INTRODUCTION

CARBON is one of the elements for which the thermionic data hitherto obtained are somewhat unsatisfactory. Thus for the constants A and ψ in the emission formula

$$i = AT^2 e^{-\psi/kT}$$

Langmuir⁽¹⁾ in 1913 obtained the values

$$\rho A = 5 \times 10^{-4} \text{ amp./cm}^2\text{-deg}^2, \psi = 2.5 \text{ eV.},$$

where ρ represents the roughness factor for the emitting surface. Such a small value for ρA is altogether improbable in view of the values that have been obtained for other clean emitters, and it seems likely that the surface of Langmuir's specimen was not really clean. A few years later, Langmuir⁽²⁾ obtained a value of 3.88 eV. for ψ , as against his previous 2.5 eV. , but no value was given for A . At about the same time, Lester⁽³⁾ measured the internal latent heat of evaporation of electrons, which, as Becker and Brattain⁽⁴⁾ have pointed out, must be the same as ψ . For this he found the value of 4.52 eV. Finally, Langmuir⁽⁵⁾, in yet another determination, has obtained the values

$$\rho A = 5.93 \text{ amp./cm}^2\text{-deg}^2, \psi = 3.94 \text{ eV.}$$

This value of ρA is much nearer the expected order of magnitude than is Langmuir's first value, but it still appears to be somewhat low. All this earlier work was carried out at a time when the need for prolonged outgassing of the filament for the removal of impurities was not realized as it is now, and so it appeared desirable to undertake a fresh study of the emission from this element.

§ 2. THE EXPERIMENTAL TUBE

The electrode system is shown in figure 1. F is a straight carbon filament 0.31 mm. in diameter and 10 cm. long, held taut by the spring S . L is a flexible lead of stranded copper wire, which carries the bulk of the filament current, only

an inappreciable fraction of it passing through the spring. Two previously outgassed nickel cylinders *C* are welded to the heavy nickel wires (also previously outgassed) to which the ends of the filaments are joined. Not only do these help to keep the nickel wires cool, but they enable them to be given a subsidiary outgassing while the tube is on the pump, by high-frequency induction heating of the cylinders. *A* is an outgassed molybdenum electron-collecting electrode of coarse mesh, 5 cm. long and of oval section measuring 3 cm. by 1.2 cm. This is separated by 5-mm. gaps at each end from two similar guard electrodes *B*, each 1 cm. long. *G* is an outgassed nickel getter cup, which holds a copper-clad barium getter pellet.

By holding the electrodes *B* as much negative with respect to the centre of *F* as *A* is positive, electrons are collected from a length of 5.5 cm. in the central region of the filament, while the emission from the remainder, near the ends, is suppressed. The object of using mesh, and not sheet, electrodes was to facilitate the escape of radiant energy from the filament and to ensure that during operation the collecting and guard electrodes should keep as cool as possible. The gaps between *A* and *B* were made relatively large with the intention of viewing the filament through one of the gaps in finding its brightness temperature as a function of heating current with the optical pyrometer. This, however, was not possible, after all, owing to the considerable blackening suffered by the walls of the tube in consequence of the deposition of nickel from the cylinders *C* during their induction heating, and so the temperature calibration was carried out subsequently, with the filament in a fresh bulb.

The carbon filament was prepared according to standard practice in the carbon-filament-lamp industry in which cellulose in the form of pure white blotting paper is dissolved in a strong solution of zinc chloride, and the viscous syrup so produced is squirted through a glass die of appropriate size into a jar of acidified alcohol. Under these conditions the cellulose is regenerated in the form of a thread, which coils itself in the alcohol. The thread is left to harden for some days and washed repeatedly until it is free from zinc chloride, and is then wound on to a large drum to dry. The dried thread is tough, and feels like a violin string. It is now set into its final shape by means of a carbon former, and the complete assembly is packed in graphite powder in a crucible and baked in a furnace to a temperature approaching 1500° C. The carbonized filament is then mounted on its nickel support wires. The ends of these are hollowed out to take the ends of the filament, and an electrically sound joint is made by passing a current through the joints while they are immersed in a bath of a hydrocarbon. The joints become very hot and the carbon deposited on them from the hydrocarbon completes the joint.

In order to ensure that the filament shall be uniform in diameter, it is next flashed, that is, heated by a current in a hydrocarbon atmosphere; heavy petroleum vapour is used. In this way irregularities are removed, since the thinner parts of the

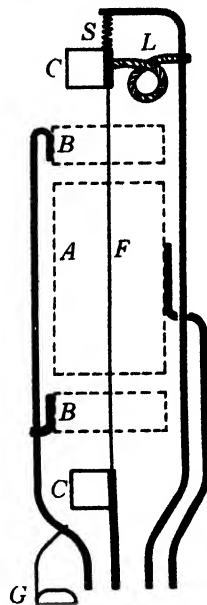


Figure 1. The electrode system.

filament are raised to a higher temperature than the rest and so receive a thicker deposit of carbon from the vapour. In this flashing process, the filament as a whole is heated to a temperature of 1600° to 1800° C., and it is left with a thin superficial coating of deposited carbon.

§ 3. TEMPERATURE CALIBRATION

After the thermionic measurements (to be discussed below) had been carried out, the tube was broken open and the filament was mounted in a fresh bulb, also provided with a barium getter. This was pumped, baked, gettered and sealed off

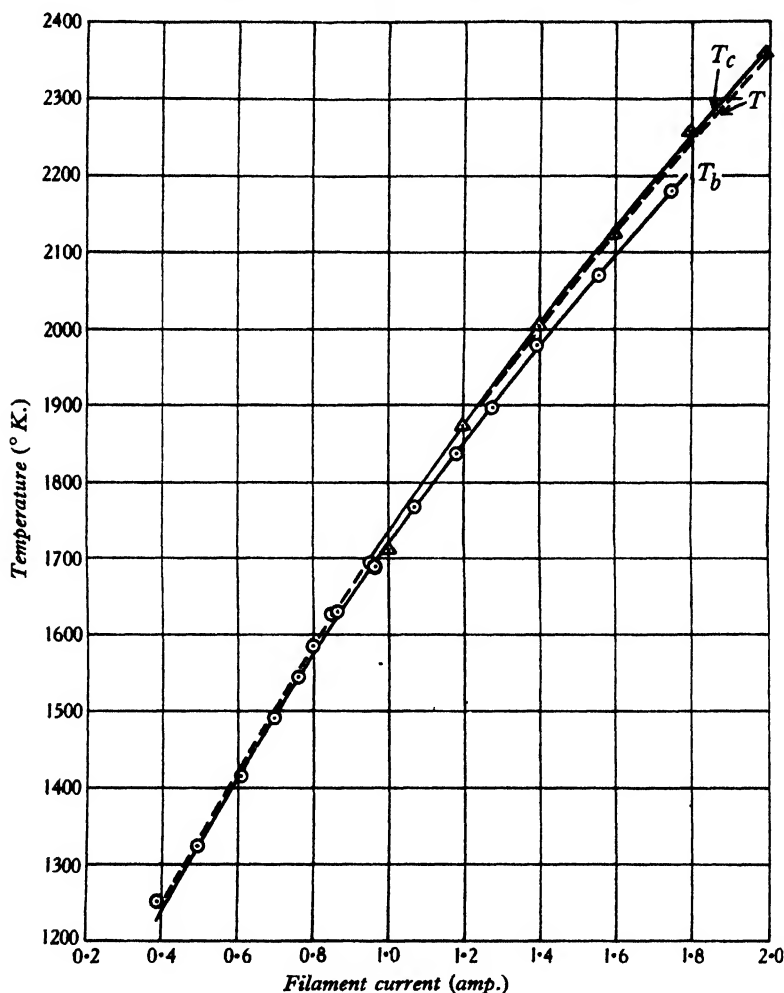


Figure 2. Temperature calibration.

in the usual manner, and then used for temperature calibration. Both brightness temperature (for a wave-length of 0.66μ .) and colour temperature were determined as a function of heating current. To increase the accuracy of the former measurements

the filament of a tungsten strip lamp, heated to various temperatures, was used as a background for the carbon filament, and the proper allowance was made for absorption and reflection by the carbon-filament bulb.

The results are shown in figure 2. The curves for brightness and colour temperature are marked T_b and T_c respectively. The true temperature is represented by the dashed curve marked T . This was obtained from the T_b curve and the spectral emissivity of graphitic carbon as found by Prescott and Hincke⁽⁶⁾. The T_c curve serves as a rough check on the curve for T . It is a general rule that the true temperature is much closer to the colour temperature than it is to the brightness temperature, and this applies to the present curves.

Furthermore, for some metals at least, for instance, tungsten⁽⁷⁾, molybdenum⁽⁸⁾, tantalum⁽⁸⁾, and niobium⁽⁹⁾, T is intermediate between T_b and T_c . It is interesting to note that the T curve in figure 2 divides the interval between T_b and T_c everywhere in very nearly the same ratio as it does in the case of these four metals.

§ 4. THERMIONIC EMISSION

The tube used for thermionic emission measurements was baked for 30 min. at 400° C. on the pump. Then, with the filament running at about 2000° K., the molybdenum electrodes and the nickel cylinders were heated by high-frequency

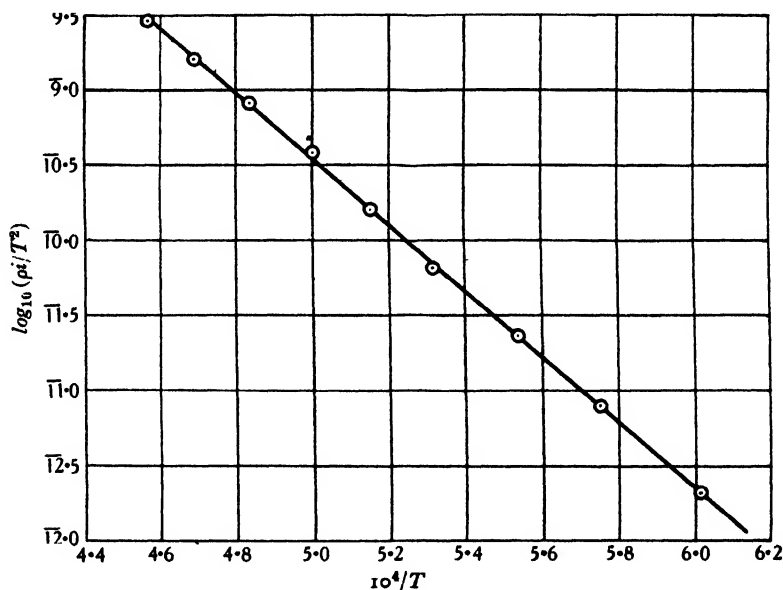


Figure 3. Richardson line for carbon.

induction to bright redness, and at the same time the getter cup G was heated just not sufficiently strongly to disperse the getter. The filament was left burning for a total of 30 min. after the induction heating, and then it was flashed for a few minutes at 2300° K. Finally, the molybdenum electrodes and the nickel cylinders were again heated to redness for a few seconds, the getter was dispersed, and the tube was

sealed off from the pump. The filament was now heated for 16½ hours at 2150° K., while, to promote the clean-up of residual gas and of any gas that might be liberated from the filament, all three molybdenum electrodes were held at 50 volts positive to its negative end, collecting an electron current of 6ma. This last heating did not bring about any important change in the thermionic activity of the filament, and so it was assumed to have attained its final, gas-free condition and the thermionic measurements were proceeded with. The emission was measured at a series of temperatures between 1665° and 2191° K. and with different applied fields at each temperature. The corresponding zero-field emissions were then calculated, Schottky's relation between emission and field being used. The results are plotted in the usual manner in figure 3. The intercept and slope of the Richardson line correspond to the values of the thermionic constants

$$\rho A = 30 \text{ amp./cm}^2\text{-deg}^2, \psi = 4.34 \text{ ev.}$$

§ 5. ACKNOWLEDGEMENTS

In conclusion, the author wishes to tender his acknowledgements to the General Electric Company and the Marconi Company, on whose behalf the work was done which has led to this publication.

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AN X-RAY STUDY OF LATTICE-DISTORTION IN RHODIUM

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ABSTRACT. Measurements of the intensities of X-ray reflections from filed and chemically prepared specimens of rhodium powder are made relatively to each other and are then converted to absolute units by comparison with suitable aluminium reflections. The scattering factors, f_T , obtained experimentally for both types of powder agree satisfactorily for the higher order reflections, with a theoretically estimated scattering factor, but for the lower order reflections the experimental values are markedly low, which suggests the existence of appreciable primary extinction. Detailed calculation shows that the variation of $[f_{T(\text{filed})}/f_{T(\text{chem.})}]$ with $(\sin \theta)/\lambda$ can be accounted for almost entirely in terms of primary extinction, and that there is very little residual effect due to lattice-distortion of the kind found in similar experiments with copper and nickel.

Measurements of the widths of the reflections are made for both types of powder; for the filed powder a total of 23 reflections for five radiations are measured. The results are discussed in relation to various theories of the nature of lattice distortion produced in metals by cold-work. The results are shown to be incompatible with the view that the broadening is due to smallness of crystal-size since the observed widths when plotted against θ fall on or near a mean curve, whereas with small crystal broadening there should be a separation according to wave-length. The difficulties attendant on any explanation in terms of periodic or semiperiodic lattice-distortion which have been discussed by Boas are briefly outlined. It is shown that the observed results may be explained in terms of a variation of the lattice spacing about the normal mean value due to the stresses caused by the filing process. Assuming a Gaussian distribution for the variation $(\delta a/a)$, the spread of the distribution is calculated. In this calculation there is only one adjustable parameter and this fixes the spread of the distribution. From this distribution a calculation is made of the internal energy of the worked metal.

§ 1. INTRODUCTION

X-RAY methods have been applied to the study of lattice-distortion in metals by considering the changes (*a*) in the intensities, and (*b*) in the widths of the X-ray reflections. A considerable amount of work has been done on this subject but hitherto, in any one investigation, attention has been focused mainly on one or other of these methods. A comparison of the results obtained by different investigators shows that conclusions drawn from intensity measurements alone as to the nature and magnitude of lattice-distortion in certain metals cannot easily be reconciled with conclusions based solely on line-width measurements; furthermore,

estimates of the latent energy in a worked metal based on the conclusions drawn from the measurements of intensities and of line-widths do not agree with each other even as regards the order of magnitude of the effect, nor do they agree with direct calorimetric measurements of the latent energy. These difficulties have been discussed in two recent papers by Boas^(2,3). The conflicting nature of these conclusions points to the desirability of a wider experimental study of the subject, and this we are attempting to supply for a selected group of metals by making both intensity measurements and line-width measurements on the same sample of metal. By making absolute measurements of the reflected intensities, we are able to obtain more definite information than is obtainable from relative measurements; in the majority of previous experiments, relative measurements only have been made.

Rhodium was chosen for detailed investigation because preliminary results had shown that, compared with a number of other metals, it gave particularly broad lines when cold worked. Moreover, since the *K* absorption edge of rhodium lies well on the short-wave side of the wave-lengths usually employed in experiments of this type, the intensity of the general scattered radiation is small compared with the intensities of the reflected lines, which thus stand out prominently against a relatively weak background.

The results of an investigation of lattice-distortion in copper and nickel by one of the writers and F. W. Spiers⁽⁶⁾ by means of X-ray intensity measurements have now been supplemented by measurements of the line-widths of the reflections carried out under the same conditions as for the rhodium measurements. These results, together with some measurements for aluminium and silver, will be discussed in relation to the rhodium results in a subsequent paper.

Throughout these experiments we have examined the distortion produced by filing the metal and have used the finest filed particles selected by a sieve with 350 meshes to the inch. In intensity measurements, filing has an important advantage over other methods of producing distortion since a specimen composed of filed particles shows little or no preferential orientation of the reflecting planes; other methods of producing distortion may result in a marked orientation which will probably have a far greater effect on the reflected intensities than the distortion itself.

The criticism may be made that filing cannot be controlled sufficiently well to justify any comparison between results from different metals. As regards the line-widths, we find that for any particular metal they are practically independent of the manner in which the filing is carried out, e.g., whether a coarse file or an almost dead smooth file is used. In view of the conclusion drawn by Wood^(20,21) that distortion produced in a metal by cold work has a limiting value which is not exceeded by continuing the cold-working process, it seems probable that the filed particles have suffered the maximum distortion possible at room-temperature. We also find that the line-widths of reflections from filed metals are comparable with the widths from metals which have been strongly worked in other ways. As regards the intensities of the reflections, they appear to depend to a small extent on the type of file used, but not to such an extent as to prevent a significant comparison of the results obtained from different metals.

§ 2. EXPERIMENTAL

The intensities of the reflections have been measured absolutely by the method of substituted powder layers described in a previous paper in these Proceedings by one of the writers and F. W. Spiers⁽⁷⁾; absolute values of the intensities have been obtained by comparison with suitable reflections from aluminium.

For the line-width measurements, photographs were taken with a camera of the type previously described having a collimator 27.5 mm. long and 0.58 mm. in diameter; the divergence of the incident radiation, measured photographically, was found to be 0.0339 radian (1.94°). In order to distinguish more satisfactorily between various possible causes of the broadening, photographs were taken with the $K\alpha$ radiations of five metals, zinc, copper, nickel, cobalt and iron; the $K\beta$ radiations were removed by suitable filters. The plate of powder was set at an angle α equal to 50° with the incident radiation; this setting gave a convenient range of reflections with all the radiations employed and was used for all the line-width measurements.

The filed rhodium was prepared from a fused button of the metal supplied by Messrs Johnson, Matthey and Co. Ltd. The line-widths and intensities corresponding to the undistorted metal were obtained from measurements on a fine powder produced by chemical reduction. The files used were of Swiss make of no. 4 and no. 6 grades of fineness; the no. 4 file is moderately smooth, the no. 6 almost dead smooth.

The X-ray photographs were measured with a Cambridge microphotometer by a null method. Readings were taken of the density of photographic blackness at intervals apart equal to 0.0185 mm. over each reflection and 0.0370 mm. along the background at each side of the reflection. For each reflection 20 or 30 readings were taken on the background at each side of the line, and 50 or more readings over the line. Two or three independent runs were made for each reflection on each film, and usually about 10 films were taken to obtain a final average value. As measures of the widths of the lines we have taken (a) the width at half the maximum intensity, and (b) the width as defined by von Laue⁽¹⁷⁾, namely the integrated intensity divided by the maximum intensity. These widths will be termed "half-widths" and "Laue widths" respectively.

§ 3. RESULTS OF THE INTENSITY MEASUREMENTS

Two series of measurements have been carried out. In the first the intensities from the filed powders were compared with the corresponding intensities from the powder prepared chemically. In the second series the intensities from the chemically prepared powder were placed on an absolute scale by comparison with suitable aluminium reflections. The results are conveniently expressed in terms of the atomic scattering factor f_T (the suffix T denotes a measurement at room-temperature T) which is derived from the integrated intensity, I_r , of a reflection by the following relation:

$$I_r/A = C \cdot pF^2 \cdot \phi(\theta),$$

where F , the scattering factor per unit cell, is equal to $4f_T$ for face-centred cubic metals,

$$\phi(\theta) = (1 + \cos^2 2\theta) / (\sin \theta \cdot \sin 2\theta)$$

and

$$A = [\sin(2\theta - \alpha)] / [\sin(2\theta - \alpha) + \sin \alpha],$$

where θ is the angle of reflection and α the angle between the incident radiation and the powder-surface, p is the multiplicity factor, and C is a constant.

Table 1 gives the measured values of the ratio of the scattering factors of the filed and chemically prepared powders calculated from the relation

$$f_{T(\text{filed})} / f_{T(\text{chem.})} = [I_{r(\text{filed})} / I_{r(\text{chem.})}]^{\frac{1}{2}}$$

for the two specimens of filed powders. The results are plotted against $(\sin \theta) / \lambda$ in figure 1 where the circles and squares correspond to powders prepared with grade 4 and grade 6 files respectively; the vertical line attached to each point indicates the mean deviation of the observed values from the mean value. The dashed lines are mean curves through the experimental results.

Table 1. Ratio of the scattering factors of filed and chemically prepared rhodium powders

Reflections	$(\sin \theta) / \lambda$	$f_{T(\text{filed})} / f_{T(\text{chem.})}$	
		no. 4	no. 6
111	0.228	0.93 ₁	0.96 ₄
200	0.263	0.84 ₂	0.85 ₄
220	0.373	0.87 ₅	0.92 ₁
311	0.437	0.88 ₆	0.93 ₄
331	0.574	0.93 ₃	0.94 ₃
420	0.589	0.92 ₇	0.95 ₃

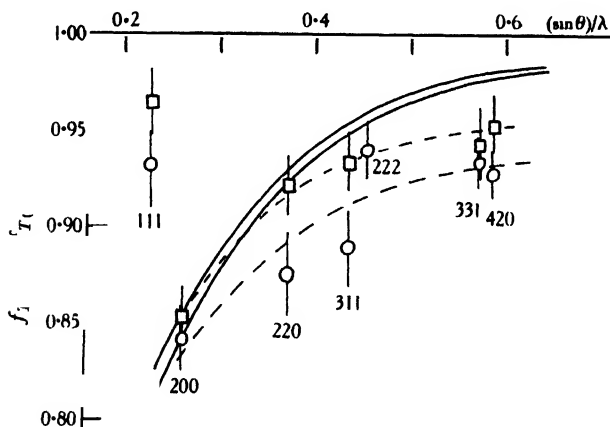


Figure 1. Dashed lines show the observed variation of $f_{T(\text{filed})} / f_{T(\text{chem.})}$ with $(\sin \theta) / \lambda$; the full lines show the calculated variation assuming primary extinction in the powders. The circles are the observed values for the no. 4 powder, obtained with the coarser file, and the squares for the no. 6 powder.

Absolute values of f_T^* were obtained for all the specimens and are set out in table 2. Column 3 of the table gives the values of f_T for the chemical rhodium powder together with the aluminium reflections used as standards. The values of f_T assumed for the aluminium reflections are those given previously by the writers; see column 4 of table 1 in reference (8). The calculation of the results is based on equation (3) of the paper by Brindley and Spiers⁽⁷⁾. In columns 4 and 5 are given the values of f_T for filed rhodium calculated from the ratios in table 1 and the values of f_T for the chemical powder in column 3.

Table 2. Absolute values of f_T for filed and chemically prepared rhodium powders, and theoretical values of f_T for the rhodium atom

1	2	3		4	5	6
Reflec- tions	$(\sin \theta)/\lambda$	Absolute values of f_T , experimental		Filed rhodium no. 4	Filed rhodium no. 6	Theoretical $f_T = (f - \Delta f) e^{-M}$
		Chemical rhodium	Aluminium reflections used as standards			
111	0.228	28.5	111, 200	26.5	27.5	32.2
200	0.263	27.4 ₈		23.1	23.4 ₈	30.2
220	0.373	23.5 ₈		20.6	21.7	24.7
311	0.437	21.8	220, 311	19.4	20.3 ₈	22.2
222	0.456	21.3		—	—	21.5 ₈
331	0.574	18.7		17.4 ₈	17.6 ₈	18.2
420	0.589	18.3		16.9 ₈	17.4 ₈	17.8
422	0.645	16.6 ₈		—	—	16.4 ₈

§ 4. THEORETICAL SCATTERING FACTOR OF RHODIUM

To ascertain whether the values of f_T for the chemically prepared powder are affected by extinction, we have estimated a theoretical scattering factor, f , in the following way. The only element near rhodium for which the electron-distribution has been calculated by Hartree's method is Ag^+ for which the calculations have been made by Miss Black⁽¹⁾. In table 3, column 2, values of f are given for Ag^+ calculated from Miss Black's results, and in column 3 are given the more approximate Thomas-Fermi values for neutral silver; the ratio of the Hartree to the Thomas-Fermi values is given in column 4 and differs from unity by less than 3 per cent between $(\sin \theta)/\lambda = 0.1$ and 0.7. We have therefore estimated f values of

* It has previously been pointed out that a weakness of the so-called substitution method of obtaining absolute values of f_T arises from the necessity of knowing the coefficients of linear absorption, μ , of the radiation in the two substances and this difficulty is apparent in the present case for no measurements of μ for rhodium for copper $K\alpha$ radiation have been made. To test the reliability of Jonsson's method of estimating absorption coefficients for elements in this region, we have compared the values given by Jonsson's method for silver with the following experimental values for the mass absorption coefficient μ/ρ : 217 (Allen), 212 (Jonsson), 214 (Barkla and Sadler); the mean of these, 215, is probably correct to about 1 per cent. Jonsson's interpolation method gives $\mu/\rho = 223$, which is about 4 per cent higher than the mean experimental value. We have therefore assumed that the method will give a value for rhodium also 4 per cent too high and have therefore taken μ/ρ equal to 190 for rhodium for copper $K\alpha$ radiation. For the density ρ we have taken 12.41 as given by Owen and Yates. Since f_T depends on $\sqrt{\mu}$, the percentage error in f_T will be only half that in μ , and since μ for rhodium is unlikely to be in error by more than 2 per cent, the error in f_T on this account is unlikely to be more than 1 per cent.

the Hartree type for rhodium by multiplying the Thomas-Fermi values for rhodium by the ratio of the Hartree to the Thomas-Fermi values for silver. This procedure is admittedly lacking in rigour but it probably gives a better approximation to the true values of f than the unmodified Thomas-Fermi values.

To compare the theoretical values of f with the measured values of f_T , we must make allowance for the heat motion in the lattice and for the effect of dispersion. With the usual notation we have

$$f_{T, CuK\alpha} = (f_{\lambda \rightarrow 0} - \Delta f) e^{-M}$$

where $f_{\lambda \rightarrow 0}$ is the theoretical scattering factor valid for short waves, Δf is the dispersion term which for rhodium and copper $K\alpha$ radiation has the value 1.27 according to Hönl's method of calculation⁽¹⁴⁾, and e^{-M} is the heat-motion factor calculated from the characteristic temperature Θ which for rhodium is 370° K. The values of f_T for copper $K\alpha$ radiation obtained in this way are given in column 6 of table 2.

Table 3. Values of f for silver and rhodium

1	2	3	4	5	6
$(\sin \theta)/\lambda$	f for silver			f for rhodium	
	Hartree	Thomas-Fermi	Hartree Thomas-Fermi	Thomas-Fermi	Hartree (estimated)
0.0	46.0	47.0	—	45.0	—
0.1	43.4	43.0	1.010	41.1	41.5
0.2	37.5	36.9	1.016	35.1	35.7
0.3	31.7	31.3	1.015	29.8	30.2
0.4	27.1	26.8	1.014	25.4	25.7 ₅
0.5	23.9	23.7	1.005	22.6	22.7
0.6	21.4	21.3	1.006	20.2	20.3
0.7	19.5	19.0	1.027	18.0	18.5
0.8	17.8	17.0	1.047	16.1	16.8 ₅

§ 5. DISCUSSION OF THE RESULTS OF THE INTENSITY-MEASUREMENTS

The data in columns 3 and 6 of table 2 show that the measured values of f_T for the chemical powder agree well with the theoretical values for the higher-order reflections but fall below the theoretical values for the lower-order reflections. This effect is almost certainly due in part, if not wholly, to primary extinction. Darwin⁽¹⁰⁾ has shown that to a close approximation primary extinction reduces the reflected intensity according to the relation

$$\frac{I_{\text{r (with extinction)}}}{I_{\text{r (without extinction)}}} = \frac{\tanh xq}{xq},$$

where

$$q = \frac{n\lambda}{\sin \theta} \frac{Fe^2}{mc^2}.$$

In these expressions, q is the reflected amplitude per lattice plane, n the number of unit cells per unit area, x the number of planes taking part in the reflection, and the remaining symbols have their usual significance. If d is the spacing of the planes

and N the number of cells per unit volume, then $n = Nd$. Further, if L is the thickness of the crystal normal to the reflecting planes and a the side of the unit cube of the structure, then $x = L/d$ and $N = 1/a^3$; also $F = 4f_T$. Hence

$$xq = \frac{4f_T e^2}{mc^2 a^3} \left(\frac{\lambda}{\sin \theta} \right) L.$$

We wish to consider first how far the observed variation of $f_{T(\text{filed})}/f_{T(\text{chem.})}$ with $(\sin \theta)/\lambda$ shown by the broken curves in figure 1 can be accounted for in terms of primary extinction. Since f_T is proportional to $\sqrt{I_r}$, we have

$$\frac{f_{T(\text{filed})}}{f_{T(\text{chem.})}} = \left(\frac{\tanh xq}{xq} \right)^{\frac{1}{2}}_{\text{filed}} / \left(\frac{\tanh xq}{xq} \right)^{\frac{1}{2}}_{\text{chem.}}.$$

To evaluate the right-hand side of this equation, we require to know the crystal-sizes L of the powders, and also f_T . Values of L may be obtained by assuming for one particular reflection that the whole of the drop of f_T below the calculated value of f_T is due to primary extinction. In calculating xq we must use values of f_T which are free from extinction, and we have therefore used the theoretical values. When the quotient of $(\tanh xq)/xq$ for the filed and chemical powders is taken, small errors in f_T and L will tend to cancel out and the final result will therefore be more accurate than the values of $(\tanh xq)/xq$ for the separate powders.

The mean crystal sizes L calculated from the data for the 200 reflection, are as follows:

For the chemically prepared powder 3.45×10^{-5} cm.

For the filed powder, grade 6 6.35×10^{-5} cm.

For the filed powder, grade 4 6.65×10^{-5} cm.

The calculated results for $f_{T(\text{filed})}/f_{T(\text{chem.})}$ plotted against $(\sin \theta)/\lambda$ are shown by the full lines in figure 1; their general run is similar to the run of the experimental points, but the latter fall below the calculated curves as $(\sin \theta)/\lambda$ increases. The percentage difference between the observed and calculated values is, however, small for all reflections except the 111. The agreement between them could be improved by making some allowance for the distribution of crystal-sizes about the mean values given above, but it would not be profitable in the present case to carry out such calculations in detail because the agreement is already fairly close when average values of L are used; and, secondly, the accuracy of the measurements, although as high as can reasonably be expected under the conditions imposed by the breadth of the lines from the filed powders, is not so high as to justify a more detailed calculation. It seems reasonable to conclude from these results that the major part of the variation of $f_{T(\text{filed})}/f_{T(\text{chem.})}$ with $(\sin \theta)/\lambda$ can be attributed to primary extinction.

The abnormal values obtained for the 111 and 222 reflections are almost certainly connected with the fact that the {111} planes are the planes on which slip occurs most readily in face-centred cubic metals. This might result in L being less for the {111} planes than for the other planes and might also give rise to a tendency for the {111} planes of the filed powder to be aligned parallel to the powder surface.

Measurements were not at first made on the relatively weak 222 reflection from the filed powders but the peculiarity of the results for the 111 reflection led us afterwards to measure the 222 reflection from the no. 4 filed powder, but it was not deemed necessary to make the measurement for the no. 6 powder also.

The fact that the experimental results for the powder obtained with the no. 6, the smoother, file are higher than for the no. 4 file also points to primary extinction being the cause of the difference between the values of f_T for the filed and chemical powders. The finer file required a very much greater expenditure of energy to yield sufficient powder; presumably the crystal-size of the powder was reduced more by this file than by the no. 4 file, but there is no evidence for any greater distortion in the no. 6 powder.

A comparison of the present results with those previously obtained by Brindley and Spiers⁽⁶⁾ for copper and nickel will be considered in detail in a subsequent paper, and it will be sufficient to mention briefly here that there is a marked difference between the rhodium results and those for copper and nickel. Whereas for copper and nickel, $f_{T(\text{filed})}/f_{T(\text{chem.})}$ decreased as $(\sin \theta)/\lambda$ increased and there appeared to be little or no primary extinction, with rhodium practically the whole of the variation of $f_{T(\text{filed})}/f_{T(\text{chem.})}$ with $(\sin \theta)/\lambda$ can be explained in terms of primary extinction, and there seems to be little or no residual effect which might be attributed to lattice distortion.

§ 6. RESULTS OF LINE-WIDTH MEASUREMENTS

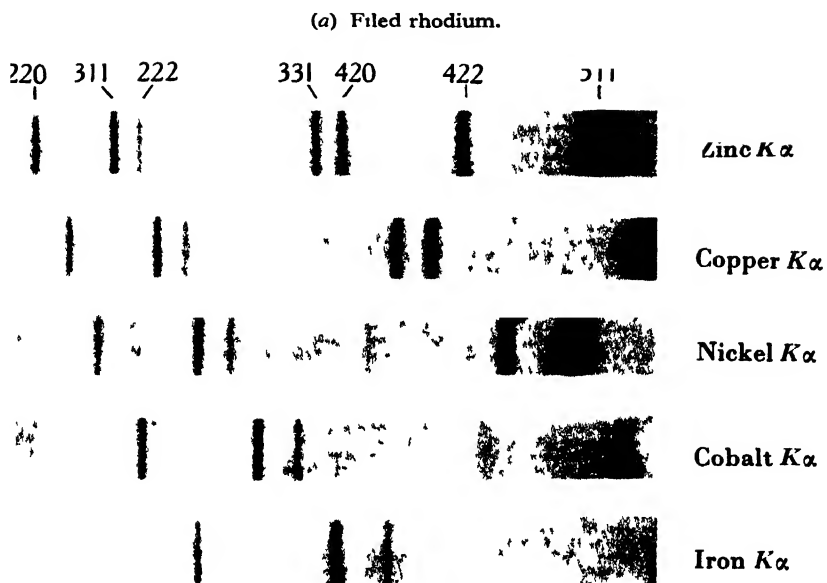
Preliminary measurements with copper $K\alpha$ radiation showed that there was no measurable difference between the widths of the reflections from the two specimens of filed powder; a full set of measurements with the $K\alpha$ radiations of zinc, copper, nickel, cobalt and iron were therefore made for the grade 4 powder only. For the chemically prepared powder it was found unnecessary to use more than two radiations; zinc and copper $K\alpha$ radiations only were used.

The results are summarized in table 4. Both the Laue widths and the half-widths of the reflections were measured, but as they differ only slightly one series of widths only is recorded; the Laue widths are given since theoretical calculations involving widths of reflections are almost invariably based on Laue's definition of line-width. As would be expected, the Laue widths are slightly larger than the half-widths, being 10 per cent larger for reflections from the filed powder and 5 per cent larger for reflections from the chemical powder.* Photographs obtained with the filed and chemically prepared powders for the various radiations are reproduced in plate 1.

Each reflected line contains two components, $K\alpha_1$ and $K\alpha_2$, the separation of which varies with the $K\alpha$ radiation used and with the angle θ . By differentiation of the Bragg equation, we have for the linear separation of the two components

$$\delta = 2R \cdot \Delta\theta = 2R \tan \theta \Delta\lambda/\lambda,$$

* If we assume a reflected line to have a Gaussian distribution of intensity of the type $I = I_0 e^{-a^2 x^2}$, then it is easily shown that the half-width is $2\sqrt{\log_e 2}/a$ and the Laue width is $\sqrt{\pi}/a$, so that the ratio of the Laue width to the half-width is $(\pi/\log_e 2)^{1/2}$, which is 1.064.



(b) Chemically prepared rhodium.

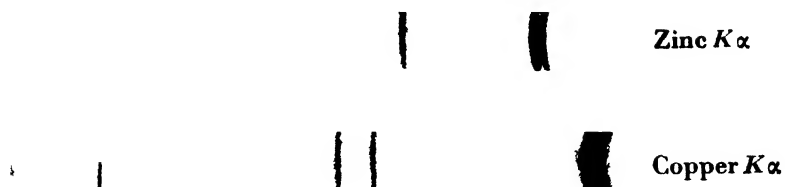


Plate 1 Reflections from filed and chemically prepared rhodium powders for various radiations.

where R is the radius of the film, $2\Delta\theta$ is the angular separation of the reflected components, and $\Delta\lambda$ is the difference in the wave-lengths of the components. Values of δ are given in millimetres in column 5 of table 4 and are calculated for $R = 30.5$ mm.

Table 4. Laue widths of X-ray reflections from filed and chemically prepared rhodium powders

ion	2 Reflec- tion	3 θ (degrees)	4 Laue width (mm.)	5 Separation of $\alpha_1\alpha_2$ components, δ (mm.)	6 Correction for $\alpha_1\alpha_2$ separation	7 Corrected Laue width (mm.)
(a) Filed rhodium powder						
Zinc $K\alpha$	220	32.3	0.71	0.104	0.978	0.69
	311	38.8	0.68	0.132	0.958	0.65
	222	40.9	0.61	0.142	0.938	0.57
	331	55.4	0.92	0.238	0.925	0.85
	420	57.6 _s	1.02	0.259	0.928	0.95
	422	67.7	1.39	0.400	0.908	1.26
$K\alpha$	511	79.0	2.90	0.844	0.906	2.63
	220	35.0	0.66	0.106	0.972	0.64
	311	42.2 _s	0.69	0.138	0.955	0.66
	222	44.6 _s	0.64	0.150	0.937	0.60
	331	62.1 _s	1.14	0.288	0.927	1.06
Nickel $K\alpha$	420	65.0 _s	1.34	0.327	0.933	1.25
	220	38.1	0.63	0.111	0.965	0.61
	311	46.4	0.73	0.149	0.952	0.69
	222	48.1	0.68	0.158	0.940	0.64
	331	72.0	1.78	0.436	0.932	1.66
Cobalt $K\alpha$	420	77.4	2.63	0.634	0.934	2.45
	220	41.7 _s	0.64	0.119	0.961	0.62
	311	51.3	0.87	0.166	0.958	0.83
Iron $K\alpha$	222	54.6	0.81	0.187	0.940	0.76
	220	46.1	0.73	0.129	0.964	0.70
	311	57.7	1.02	0.196	0.958	0.98
	222	62.0	1.05	0.234	0.942	0.99
(b) Chemically prepared powder						
Zinc $K\alpha$	220	32.3	0.49	0.104	0.949	0.46
	311	38.8	0.38	0.132	0.870	0.33
	222	40.9	0.35	0.142	0.822	0.29
	331	55.4	0.49	0.238	0.757	0.37
	420	57.6 _s	0.51	0.259	0.746	0.38
	422	67.7	0.69	0.400	0.718	0.49 _s
Copper $K\alpha$	220	35.0	0.45	0.106	0.937	0.42
	311	42.2 _s	0.38	0.138	0.858	0.33
	222	44.6 _s	0.38	0.150	0.831	0.31 _s
	331	62.1 _s	0.60	0.288	0.761	0.45 _s
	420	65.0 _s	0.66	0.327	0.751	0.49 _s
(c) Widths of resolved lines from chemically prepared powder						
Zinc $K\alpha$	511 α_1	78.6	0.55	—	—	—
	511 α_2	79.4	0.53	—	—	—
Copper $K\alpha$	422 α_1	82.7	0.68?	—	—	—
	422 α_2	84.0	0.66?	—	—	—

An expression for correcting observed Laue widths for $\alpha_1\alpha_2$ separation has been calculated by Brill⁽⁴⁾ on the assumption that the intensities of the α_1 and α_2 components are in the ratio of 2 : 1 and that the distribution of intensity in a reflected line has a simple triangular shape. Neither assumption is fully justified and the latter is especially doubtful. A graphical test of the accuracy of Brill's formula for lines of the shape obtained in our work was made and it was found that for small values of δ the formula gave corrected widths as much as 4 per cent too small, and for larger values of δ as much as 5 per cent too large; hence relative errors as large as 9 per cent might be obtained. In the meantime a more satisfactory method of correcting for $\alpha_1\alpha_2$ separation has been developed by F. W. Jones⁽¹⁵⁾ and a short abstract describing it has appeared;* the method is a graphical one and the writers are much indebted to Dr Jones for supplying them with details of this work prior to their full publication. The correction factors given in column 6 of table 4 are based on the data supplied by Dr Jones and the corrected Laue widths are given in column 7 of the table.

Section (a) of table 4 refers to results for filed rhodium and section (b) to those for chemically prepared rhodium. Section (c) gives results for two high-order reflections from the chemical powder for which the α_1 and α_2 components are clearly resolved. These reflections also enable us to measure the intensities of the α_1 and α_2 components, which we find to be in the ratio 1.84 : 1 for zinc radiation and 1.80 : 1 for copper radiation. These are the ratios of the intensities recorded on the film which will be slightly different from the ratio of the intensities in the incident beam owing to the different absorption of the components. The Laue widths of the 422 α_1 and α_2 reflections with copper radiation are regarded as doubtful owing to a possible shielding of the background on one side of the lines by the collimator.

In figure 2 the Laue widths, after correction for $\alpha_1\alpha_2$ separation, are plotted against the angle θ ; the results obtained with different radiations are shown by the use of different symbols. For the chemical powder the results lie close to a single mean curve. For the filed powders there is a greater divergence of the values from a mean curve, but with the exception of the results for the 222 reflections, which are consistently low, the great majority of the remaining points lie on or near a mean curve; as will be seen in the next section, this fact is of special importance in the interpretation of the results.

§ 7. DISCUSSION OF THE LINE-WIDTH MEASUREMENTS

We will now examine the results of the line-width measurements in relation to the various explanations which have been suggested to account for the broadening of the reflections caused by cold working. Since crystals of sizes approaching colloidal dimensions are known to give broadened lines, it has often been put forward as a possible explanation that cold working may produce crystals sufficiently small to yield broadening of this type. On the other hand the broadening might be explained by some type of lattice distortion such as that considered by Dehlinger⁽¹¹⁾

* Note added in proof. The full account of Dr Jones' work has just appeared, *Proc. Roy. Soc. A*, **166**, 16 (1938).

and Boas⁽³⁾ in particular. A further possibility is that the stresses set up by the cold working may lead to extensions and compressions of small regions of the metal and so cause small deviations from the normal lattice spacing. We will consider these three kinds of explanation in turn.

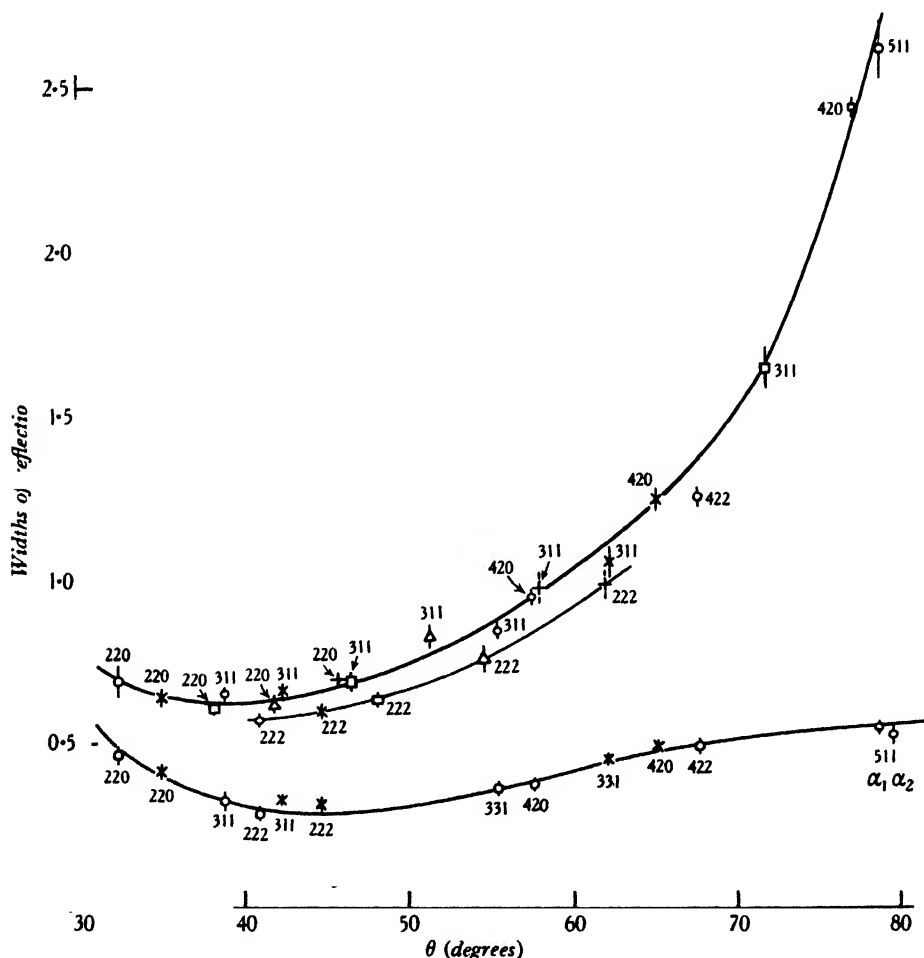


Figure 2. Laue widths of reflections, after correction for $\alpha_1 \alpha_2$ separation, plotted against θ . The lower curve is for chemically prepared rhodium powder, the upper curves are for the filed powder. Except for the 222 reflections the widths from the filed powder lie on or near the mean curve; a slightly lower curve passes through the points representing the 222 reflections. The symbols indicate the radiations employed: O, zinc $K\alpha$; x, copper $K\alpha$; □, nickel $K\alpha$; Δ, cobalt $K\alpha$; +, iron $K\alpha$.

(a) *Line-broadening due to small crystals.* The theory of line-broadening by small crystals was first considered by Scherrer⁽¹⁸⁾ who derived the following equation for cubic crystals and parallel or nearly parallel radiation:

$$\frac{W}{R} = 2 \frac{\lambda \sec \theta}{L} \sqrt{\log}$$

where W is the linear half-width, R the camera radius, L the length of an edge of the crystal, and b a constant. From this it appears that the line-width should vary linearly with λ for a given value of θ , and it was to test this point that a number of radiations were used. A more general analysis by von Laue⁽¹⁷⁾ for cylindrical powder specimens and divergent radiation has recently been extended by Kochendörfer⁽¹⁶⁾ to the case of a flat powder layer at the centre of a cylindrical camera, and his formula for the linear Laue width W may be written

$$W = \pi r [\sin \alpha - \sin (2\theta - \alpha)] / \gamma$$

where

$$\tan \gamma = \frac{\omega}{4} \left(\frac{r}{R\eta} \right) \frac{\sin 2\theta}{\sin \theta} [\sin \alpha - \sin (2\theta - \alpha)];$$

$2r$ is the total spread of the radiation on the powder surface, ω is a constant in von Laue's theory and has the value 0.55, α is the angle of incidence of the radiation on the powder-surface, and η stands for an expression which for equiaxed cubic crystals has the value $\lambda/4\pi L$. This expression for W reduces to the same form as Scherrer's expression if γ is so small that $\tan \gamma \approx \gamma$, but under the conditions of the present experiments this approximation is not possible and the full expression must be used. Values of L calculated by applying Kochendörfer's formula to the observed widths are set out in table 5; the values show a large variation, but for the higher-order reflections L is approximately constant and of the order of 90 Å. A more useful result is obtained by carrying out calculations in the reverse manner; assuming a crystal size L equal to 90 Å. we have calculated from Kochendörfer's formula the variation of the reflected widths over the range of angles used for the different radiations. The results of this calculation are shown by the full curves in figure 3; they indicate a marked dependence of the widths on the wave-length λ of the radiation. The experimental results are shown by different symbols for the various radiations used and the dashed lines are mean curves through the experimental points.

Table 5. Values of L , in angstroms, for filed rhodium powder calculated from Kochendörfer's formula

Reflection	220	311	222	331	420	422	511
Radiation							
Zinc $K\alpha$	*	490	271	86	84	93	80
Copper $K\alpha$	*	127	119	97	89	—	—
Nickel $K\alpha$	*	101	108	95	87	—	—
Cobalt $K\alpha$	185	95	117	—	—	—	—
Iron $K\alpha$	116	109	131	—	—	—	—

* For these reflections Kochendörfer's formula gives negative values.

Figure 3 shows that the experimental results are not dependent on wave-length as they would be if the broadening were due to small crystals, and hence provides strong evidence that the broadening arises from some other cause.

In addition to this evidence, we have the fact that if the crystal-size were really of the order of 90 Å., then primary extinction would be negligible. The impossibility of reconciling the large extinction effect shown by the filed powders with a crystal-size small enough to produce broadening of the observed magnitude is additional confirmatory evidence that the broadness is not produced by small crystals.

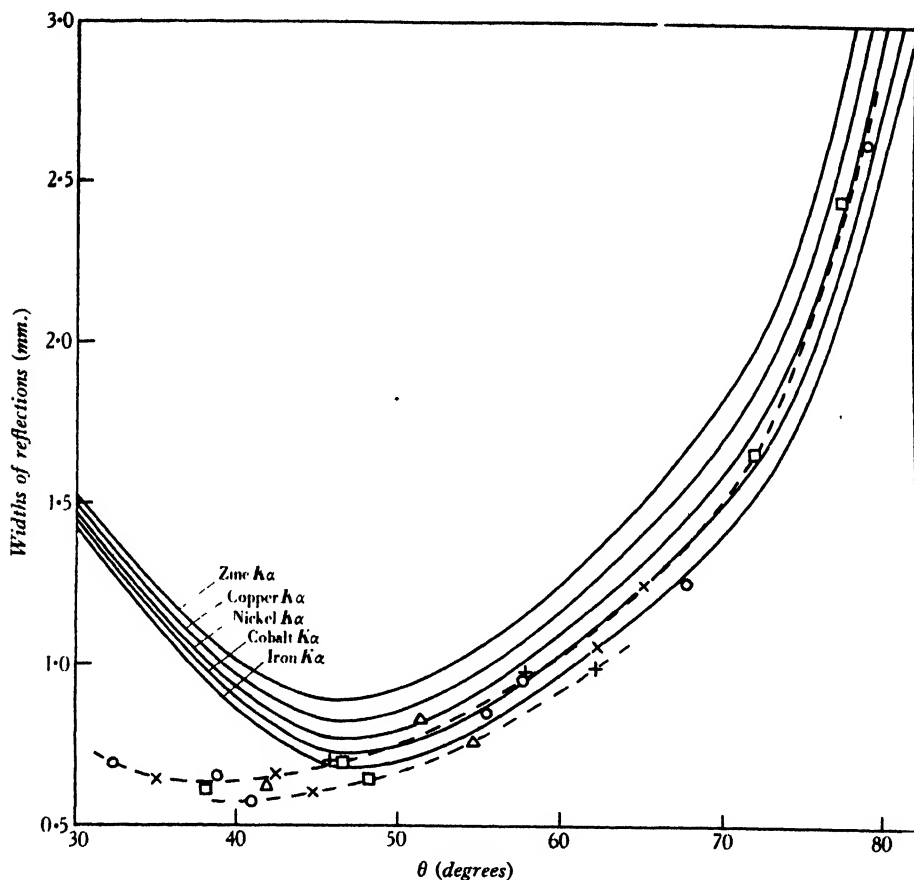


Figure 3. A comparison of the observed widths of reflections with calculated values derived from Kochendörfer's formula for the dependence of line-width on crystal size. The full lines show the calculated values for the five radiations employed and the symbols \circ , \times , \square , Δ and $+$ show the observed values for the $K\alpha$ radiations of zinc, copper, nickel, cobalt and iron respectively. The point of particular importance shown by the figure is that there is no separation of the observed values with wave-length, of the kind obtained theoretically, and therefore that the broadening of the lines does not arise from smallness of crystal-size.

(b) *Line-broadening due to lattice-distortion.* The effect of various types of lattice-distortion on the widths and intensities of X-ray reflections has been studied by Dehlinger⁽¹¹⁾ and by Boas⁽³⁾. Dehlinger showed that distortions of a strictly cosine type running throughout the lattice would give line-broadening of the magnitude observed. He also considered a type of deformation in which after each wave of distortion there is a region free from distortion; this type of deforma-

tion was shown to give no appreciable line-broadening. Boas considered a type of distortion in which equal blocks of the lattice at regular intervals are displaced normal to the reflecting planes, and this also was found to give no line-broadening. The transition from the simple cosine deformation which gives line-broadening to the other types which give negligible broadening is analysed by Boas by a method employing Fourier analysis; he shows that whereas broadening is produced by a single term of the Fourier expansion, as more terms are added the broadening rapidly diminishes. It is clear then that unless the distortion is of a strictly cosine form, which is most unlikely to occur, line-broadening would not be expected.*

(c) *Line-broadening due to variation of lattice spacing.* Haworth⁽¹³⁾ has recently shown from a detailed study of the 311 reflections from cold-worked and annealed permalloy that the shape of the broadened line can be explained on the supposition that cold working causes a variation of lattice spacing about the normal value. Several workers, as for example Wood^(20, 22, 23) and Caglioti and Sachs⁽⁹⁾, have measured the increase of line-width for one or a small number of reflections and have correlated the increase with a mean change in the lattice spacing. Boas also has expressed the view that broadening might be connected with a variation of lattice spacing. Despite frequent reference to the possibility of a variation in lattice spacing, there does not appear to have been any extensive study of the widths from this standpoint. In the present experiments we have measured the widths of 23 reflections for five different radiations; these results are sufficiently extensive to provide a wide basis for testing the hypothesis.

By differentiation of the Bragg equation, taking the lattice spacing a and the angle θ as variables, we obtain

$$d\theta = -\tan \theta \cdot da/a.$$

Corresponding to a change δa , the reflected line is displaced a distance δx on the film given by

$$\delta x = 2R \cdot \delta\theta = -2R \tan \theta \delta a/a.$$

The shape of the broadened line will depend on the distribution of $\delta a/a$ about a mean value zero. Assuming that the distribution follows a Gaussian law, we have for the probability dp that $\delta a/a$ will lie in a small range between z and $(z + dz)$

$$dp = e^{-h^2 z^2} dz / \int_{-\infty}^{+\infty} e^{-h^2 z^2} dz = \frac{h}{\sqrt{\pi}} e^{-h^2 z^2} dz.$$

If the distribution of intensity on the film for a reflection from the chemical powder is represented as a function $I(x)$ of x , then for the worked metal a fraction $I(x) \cdot \delta p$ of this intensity will be displaced a distance δx and may be represented as $I(x') \cdot \delta p$. For numerical calculation it is convenient to replace the continuous distribution of

* Boas⁽³⁾ concludes, p. 368, "Wir glauben daher, dass die nach Deformation von Kristallen beobachtete Linienverbreiterung nicht von periodischen Gitterstörungen herrührt", and on p. 369, "Die nach plastischer Deformation auftretende Verbreiterung der Interferenzlinien ist mit periodischen Störungen des Gitters wohl nicht zu erklären. Die Linienverbreiterung dürfte zum wesentlichen Teil durch elastische Spannungen, die in grösseren Bereichen des Gitters ($\sim 0.5 \mu$) homogen sind, zustande kommen."

$d\rho$ by a series of values of $\delta\rho$ at close intervals. The intensity distribution in the broadened line is then obtained by summing the series of displaced lines of intensity $I(x')\delta\rho$.

When the breadth of the broadened line is being calculated as a function of θ , it must be borne in mind that the breadth varies with θ for two reasons; in addition to the broadening due to the variation of lattice spacing, which is approximately proportional to $\tan \theta$, there is also a broadening due to the focusing properties of the camera. We have investigated the latter by measuring the line-widths of the reflections from the chemical powder and the results are shown by the lower curve in figure 2. Using these results we can then calculate for each value of θ the width of the line resulting from any particular distribution of lattice spacings. It is to be emphasized that in calculating the widths of the broadened lines there is only one adjustable factor, namely the distribution curve, and if this is taken to be of the Gaussian type the only known quantity is h .

The result of such a calculation is shown in figure 4, where the widths are plotted against $\tan \theta$; the thin lines represent the best mean curves through the experimental points and the heavy line is the calculated curve based on a Gaussian distribution with h equal to 207. This distribution is shown in the inset of figure 4.

The agreement between the observed and calculated values is fairly close, particularly when it is considered that there is only one adjustable parameter, h . It seems justifiable to conclude that a major part at least of the broadening of the lines is caused by a variation of the lattice spacing. We have considered whether a better agreement could be obtained by modifying the distribution curve, and various departures from the Gaussian type have been examined, but it seems unlikely that any very considerable improvement could be obtained by such modification. The fact that the widths of all the reflections from the worked metal do not lie on a single curve indicates that the assumption of a single distribution curve is too simple to explain all the observations, and in view of this the agreement between the observed and calculated values is perhaps as good as can reasonably be expected.

It has been observed by Wood^(21, 22, 24) in a number of instances that some reflections show greater broadening than others: for example, the 420 reflections from copper and from α brass are broadened more than the 331 reflections. It is of interest therefore to consider whether the present measurements indicate effects of this kind. The 222 reflections lie well below the mean curve, as has already been pointed out; this result is almost certainly a consequence of the fact that slip occurs most easily on the {111} planes so that these planes would be expected to show a smaller variation in spacing than other planes. The present results point to the 420 reflections being slightly broader than the 331 reflections when considered relative to the mean curve; there is, of course, a greater absolute broadening of the 420 reflections than of the 331 reflections, due to the larger value of $\tan \theta$ for the former. This illustrates very well a point of general importance, namely that incorrect conclusions may easily be drawn from measurements of the line-widths of a small number of reflections since part of the broadening of one line with respect to another arises from the difference of $\tan \theta$ and also from the difference in the focusing

properties of the camera for the two reflections. The 311 reflections show a tendency to lie slightly above the mean curve. The 422 reflection falls well below the mean

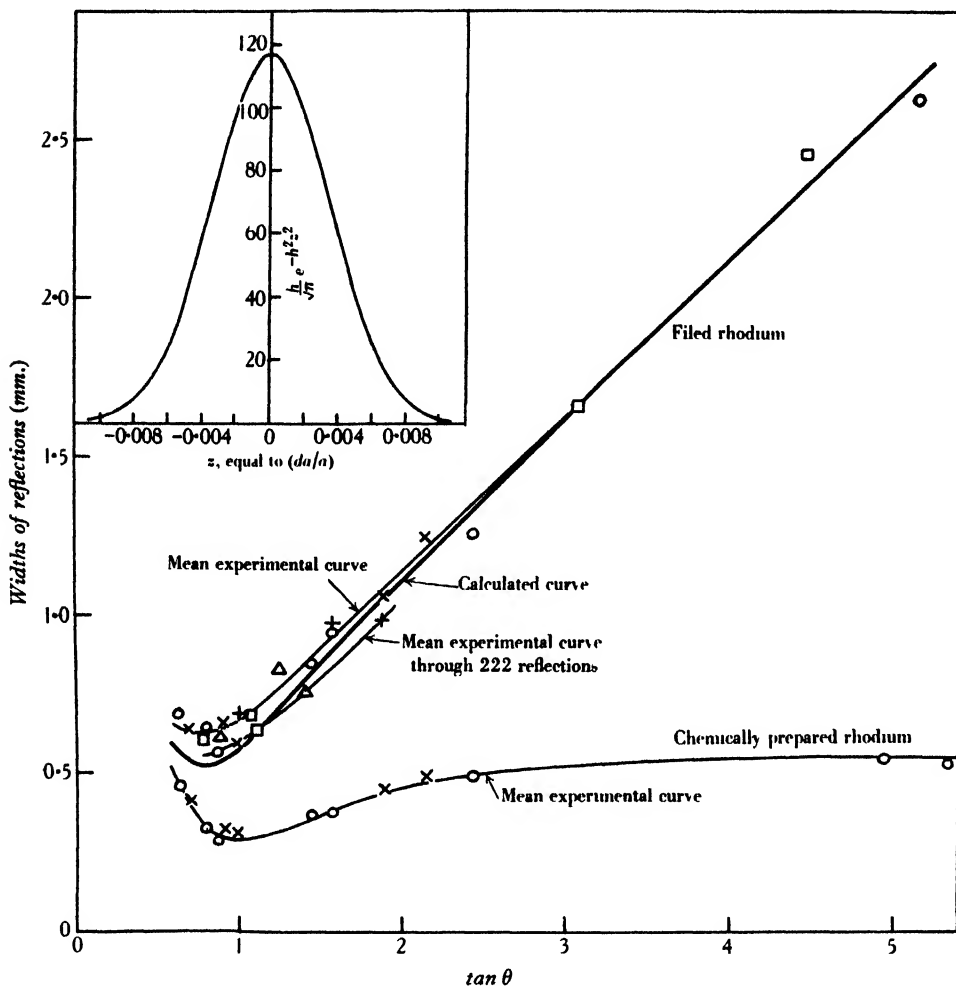


Figure 4. Reflected widths from filed and chemically prepared rhodium plotted against $\tan \theta$. The heavy curve running through the observations for the filed metal is calculated on the assumption of a Gaussian distribution of the lattice spacing about the normal mean value. The distribution is shown in the inset.

curve, but as we have only been able to measure this with zinc $K\alpha$ radiation we feel less certain of the result than in the case of the other reflections, which have been measured with several radiations.

§ 8. CALCULATION OF THE INTERNAL OR LATENT ENERGY OF DISTORTED RHODIUM

Having obtained the constant h in the Gaussian distribution, we easily obtain $|\bar{z}|$ and $\sqrt{z^2}$, where z is written for $\delta a/a$.

$$|\bar{z}| = \frac{2h}{\sqrt{\pi}} \int_0^{\infty} e^{-h^2 z^2} z dz = \frac{1}{h\sqrt{\pi}} = 0.00272$$

$$\sqrt{z^2} = \left[\frac{h}{\sqrt{\pi}} \int_{-\infty}^{+\infty} e^{-h^2 z^2} z^2 dz \right]^{\frac{1}{2}} = \frac{1}{h\sqrt{2}} = 0.00341.$$

These values are of the same order of magnitude as Haworth obtained from his study of the 311 reflection from permalloy. To calculate the internal or latent energy, Haworth uses the following formula derived by Stibitz⁽¹⁹⁾:

$$V = 3E\bar{z}^2/[2(1 + 2\sigma^2)],$$

where V is the energy per unit volume, E Young's modulus, and σ Poisson's ratio. A somewhat similar formula has been given by Boas⁽²⁾. Stibitz's formula assumes that the substance is elastically isotropic and that the stresses are independent and oriented at random with zero mean values. The experimental results themselves show that the stresses are not oriented entirely at random, so that the formula cannot strictly be applied, but nevertheless it may be used to obtain an estimate of the latent energy. Taking E as equal to 29.4×10^{11} dyne-cm.², as given by Grüneisen⁽¹²⁾, and assuming that $\sigma = 0.3$, we obtain for the energy per gram

$$V = 0.0834 \text{ cal./g.}$$

This value may be compared with the value found by Haworth for cold-worked permalloy, namely, 0.066 cal./g. It is considerably larger than values calculated by Boas for copper and nickel by a factor of the order of 20, but a larger value is to be expected for rhodium owing to its much greater hardness.

§ 9. CONCLUSIONS

The results of measurements of X-ray intensities reflected by filed and chemically prepared specimens of rhodium powder show that the change of intensity produced by working the metal may be largely explained in terms of primary extinction, and that there is little or no residual effect such as was previously found in similar experiments on copper and nickel, which might be attributed to lattice-distortion. The mean crystal-sizes of the filed powders calculated on the assumption that the whole of the variation of $[f_{T(\text{filed})}/f_{T(\text{chem.})}]$ with $(\sin \theta)/\lambda$ is due to primary extinction are found to be 6.35×10^{-5} cm. and 6.65×10^{-5} cm. respectively for the two filed powders investigated.

Measurements of the reflected widths are made for a total of 23 reflections for five radiations. It is shown that the results cannot be explained in terms of a small crystal-size, since the observed widths plotted against θ lie on or near a single mean curve, whereas if the broadening were due to small crystals a separation according

to wave-length should be obtained. Moreover, the relatively large extinction effect shown by the intensity-measurements is incompatible with a crystal-size small enough to produce broadening of the observed magnitude; a size of the order of 90 Å. would be necessary.

The observed widths are discussed in relation to other views of the nature of lattice-distribution, and it is shown that they can be accounted for reasonably well on the assumption that the lattice spacing varies about the mean normal value as a result of the internal stresses. Assuming a Gaussian distribution of the lattice spacings, a mean value of $|\langle \delta a/a \rangle|$ of 0.272 per cent, and a root-mean-square value of 0.341 per cent are found. These lead to an estimate of the internal energy of the order of 0.083 cal./g., which is to be expected from previous estimates for other metals.

§ 10. ACKNOWLEDGEMENTS

Finally we wish to thank Prof. Whiddington for his interest in these experiments, the Government Grant Committee for a grant with which the rhodium and part of the necessary apparatus were purchased, and the Department of Scientific and Industrial Research for a maintenance grant allotted to one of us (P. R.).

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THE CRYSTAL STRUCTURE OF CADMIUM-INDIUM ALLOYS RICH IN INDIUM

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ABSTRACT. The solubility of cadmium in indium has been determined by X-ray diffraction methods as 14.5 ± 0.5 atomic per cent at 100°C . and 4.5 ± 0.5 atomic per cent at 20°C . The axial ratio of the face-centred tetragonal lattice of the indium-rich solid solution has been found to decrease with increasing cadmium-content, until at 4.5 atomic per cent the structure becomes face-centred cubic. No change in the volume of the indium atom is associated with the change in axial ratio.

§ 1. INTRODUCTION

THE constitutional diagram of the cadmium-indium system of alloys has recently been determined by thermal and microscopic methods by Wilson and Wick⁽¹⁾. They found that indium dissolves cadmium, forming a solid solution; the limit of solubility is about 18 per cent at 122.5°C ., the eutectic temperature, and falls to approximately 12 per cent at room temperature. The present investigation was undertaken with the object of confirming this portion of the diagram by crystallographic methods.

§ 2. PREPARATION OF ALLOYS

The indium was supplied by Messrs Johnson, Matthey and Company, Ltd., and was stated to be of 99.98 per cent purity, the impurities being traces of copper, tin, lead and zinc, with spectroscopically visible traces of aluminium, cadmium, calcium, sodium and silver. The cadmium was obtained from the National Smelting Company, Ltd., who very kindly made a special spectroscopic analysis of the sample used, the percentages of impurities present being estimated as follows: lead 0.015, zinc 0.0075, thallium 0.0075, copper 0.004.

Owing to the high cost of the indium the alloys were made in two series starting with pure indium, additions of cadmium being made to one alloy to produce the alloy next higher in cadmium-content. The metals were melted together in a pyrex tube under a layer of mineral oil and maintained at 200°C . in an oil bath for 10 min.; this is considerably below the melting point of cadmium (321°C .) but was found to be sufficiently high for the indium to take the cadmium into solution, and had the advantage of keeping the melting losses to a minimum. The molten alloy was allowed to cool slowly to 180°C ., taking about 5 min., and the tube containing it was then removed from the oil bath and quenched in cold water, the freezing range of the alloy thereby being quickly traversed and segregation being minimized. The alloys

were all very soft and in order to render them as homogeneous as possible they were severely cold-worked by hammering and subsequently annealed at 100° C. for 3 hours. The bar of metal was then cut in two, and filings were taken from the section for examination in the X-ray diffraction camera, the residue being used as the basis for the next alloy of the series. It was found to be unnecessary to anneal the filings to remove strain, for they annealed spontaneously at room temperatures and yielded sharp high-order lines in the X-ray diffraction pattern; this also proves that the treatment given to the block of metal was efficient in yielding a sample of uniform composition.

By starting with approximately 5 grams of indium and following the procedure described above, a series of alloys was prepared with the following nominal cadmium-contents: 4.75, 8, 12, 15, 20 and 25 per cent by weight. The loss of weight in melting was between 0.005 and 0.032 g. for each alloy, corresponding to percentage losses of from 0.1 to 0.6. If the losses are assumed to consist entirely of cadmium the composition of the final alloy will be 23.3 per cent, while if the losses are entirely indium the value will be 25.2 per cent. A chemical analysis of the final alloy was made by Mr N. L. Paddock, the cadmium being estimated by precipitation with β -naphthoquinoline and the indium by precipitation with hexamine and weighing after oxidation by ignition. Two individual analyses were made, the cadmium and indium contents totalling 99.8 per cent in the worst case, and the mean result was 25.3 ± 0.1 per cent of cadmium, which suggests that the melting losses were almost entirely of indium. A fine suspension remaining in the oil used to cover the molten alloy was also found to consist mainly of indium. On these grounds it was decided that the compositions of the alloys would be most accurately represented by the values calculated on the assumption that the melting losses were entirely indium, and these values are given in the table.

Cadmium		Structure at 100° C.		Structure at 20° C.	
Weight per cent	Atoms per cent	a_0 (A.)	c/a	a_0 (A.)	c/a
0	0	4.6122 ± 0.001	1.0679 ± 0.001	4.5888 ± 0.001	1.0756 ± 0.001
0.99	1.01	4.6116	1.0668	4.5953	1.0696
1.97	2.01	4.6212	1.0589	4.5973	1.0665
2.94	3.00	4.6334	1.0497	4.6055	1.0592
3.94	4.02	4.6451	1.0397	4.6170	1.0500
4.42	4.51	4.7038 ± 0.0005	I		
4.79	4.89	4.7029	I	4.6310	1.0399
8.05	8.20	4.6939	I	4.6256	1.0434
12.06	12.28	4.6850	I	4.6302	1.0397
15.06	15.33	4.6789	I	4.6284	1.0411
20.1	20.5	4.6791	I	4.6296	1.0404
25.2	25.6	4.6799	I	4.6270	1.0424

After some results had been obtained with the first series of alloys it was found necessary to examine more alloys in the range 0 to 5 per cent of cadmium and accordingly a second series was prepared, starting with pure indium and adding the necessary amount of the 25 per cent alloy to produce alloys with the following

nominal cadmium-contents: 1, 2, 3, 4 and 4.5 weight per cent. The last alloy of this series was also chemically analysed, the cadmium-content found being 4.53 per cent, while the composition calculated from the charged weights, allowing for the losses as before, was 4.42 per cent. The compositions given in the table were calculated similarly and are considered to be accurate to within 0.1 per cent; in subsequent reference to the composition of the alloys the atomic percentages, also given in the table, are used.

§ 3. X-RAY APPARATUS AND METHOD

The X-ray apparatus used was the Philips Metalix outfit, the tube employed having a cobalt target.* The camera was 5.76 cm. in diameter and could be used both for the ordinary powder method to give a complete spectrum or for the back-reflection focusing method for accurate measurement of the high-order lines. The Debye-Scherrer method was used in preliminary observations in order to identify the lines of the diffracted pattern, but all the parameters quoted have been deduced from planar spacings obtained from photographs taken by the focusing method. A brass frame was fitted to the camera which threw a shadow of two knife edges on the film, by means of which film-shrinkage was allowed for. The distance apart of the knife edges was determined from a photograph of the reflections of pure silver, the size of the unit cell of which was taken to be 4.0773 Å.

In the case of the cubic lattice of the indium-rich solid solution the reflection of the cobalt $K\alpha$ radiation by the {333} planes of the lattice is obtained at an angle of 80 to 83°, which enables accurate evaluation of the size of the unit cell to be made. For the tetragonal lattice, however, at least two reflections are required in order to obtain the two parameters, and the following method was found to be the most accurate. The reflections from the {422} and {224} planes occur at angles of approximately 70 and 65° respectively in the case of pure indium, and approach one another as the axial ratio of the tetragonal cell is reduced, finally merging into one reflection when the cell becomes cubic. These reflections were used to calculate the axial ratio, which was then used in conjunction with the accurately determined spacing of the {333} planes to calculate the separate parameters a_0 and c_0 . The accuracy of the value of the axial ratio was twice as great when it was obtained by this method as when it was obtained by calculation from the {333} and {422} spacings, although the latter planes were those with the most accurately determined spacings.

The structures at room temperature were obtained by mounting the specimen in the form of fine filings in a uniform layer on a thin sheet of card with weak adhesive, and clamping this against the aperture in the wall of the camera. For the structures at 100° C. the filings were mounted in a similar manner on a thin metal foil, and steam was blown on to the back of the foil. No direct measurement of the temperature of the sample was made, but it has been shown by Owen and Yates (2) that a powder cemented to a metal sheet attains very closely the temperature of the sheet, and it is therefore assumed that the temperature of the sample was within 2° of 100° C. Care had to be taken to insulate the camera from the source of heat,

* The wave-lengths used were $K\alpha_1$ 1.78529 and $K\alpha_2$ 1.78919 Å.

and as a further precaution it was cooled with an air blast. It was found unnecessary to maintain the temperature of the sample for any lengthy period before commencing the exposure, for equilibrium, as judged by the sharpness of the lines in the X-ray pattern and the reproducibility of the results, was attained almost immediately. The procedure adopted was to pass steam for five minutes before commencing the exposure.

§ 4. STRUCTURES AT 100° C.

The parameters found for the indium-rich solid solution at 100° C. are given in columns 3 and 4 of the table, the values quoted being mostly the mean of two independent observations. It will be noticed that, with increasing cadmium-content, the axial ratio of the tetragonal cell falls, slowly at first and then suddenly, until at 4.5 atomic per cent of cadmium the cell becomes cubic. In figure 1 the axial ratio

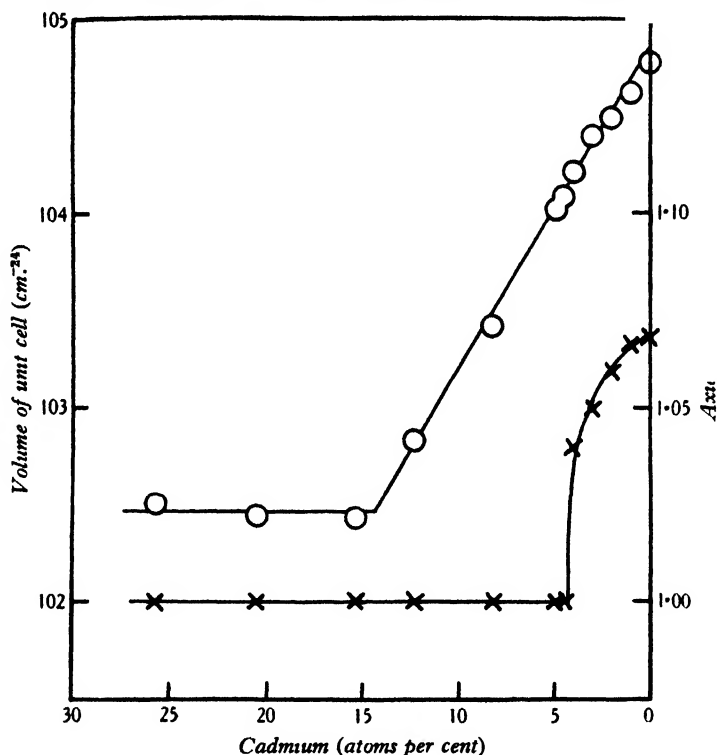


Figure 1. Cadmium-indium alloys at 100° C. O, volume of unit cell, x, axial ratio.

has been plotted against composition. The normal procedure for the determination of a solubility limit from a series of measurements such as those in the table is to plot the length of the side of the unit cell against the composition, but in the present case, in order to embrace the observations both of tetragonal and cubic lattices, the volume of the unit cell has been plotted, as shown in figure 1. From the fact that the line shows no inflection at 4.5 per cent of cadmium, the composition at which the cubic structure supersedes the tetragonal, it is clear that a true change of phase

cannot be considered to occur there, and that the tetragonal structure is, as it is usually considered to be, merely a distorted form of the normal face-centred cube, as a result of some lack of symmetry (probably incomplete ionization) of the indium atom. The true solubility limit at this temperature is at 14.5 atomic per cent of cadmium, which agrees quite well with the value of 15.3 per cent taken from the diagram of Wilson and Wick, when it is remembered that the latter investigators drew their solubility line from microscopic observations of alloys of fairly widely separated compositions.

§ 5. STRUCTURES AT ROOM TEMPERATURE

Photographs taken immediately after the samples had been cooled from 100° C. to room temperature showed that, in general, a cubic structure did not change to tetragonal, but after ageing at room temperature for several hours the tetragonal structure appeared. A gradual and slight increase in axial ratio over the range 1.035 to 1.045 was observed to proceed for several days until equilibrium was attained after about 5 days. Columns 5 and 6 of the table give the parameters obtained after all samples had been aged at room temperature for at least a week, the photographs being taken at a temperature of $20 \pm 2^\circ$ C. All the alloys have a tetragonal structure, the axial ratio falling with increasing cadmium-content until the solubility limit is reached at 4.5 atomic per cent; this limit was ascertained by plotting the volume of the unit cell against composition as before. The value is considerably lower than the 12 per cent quoted by Wilson and Wick, and the discrepancy is almost certainly due to their microscopic method not being sufficiently sensitive to detect the precipitation which occurs at low temperatures; the precipitate would undoubtedly be in a very finely divided state.

It will be noticed that the axial ratios of the alloys still in the single-phase region are consistently higher than the corresponding ratios at 100° C., even in the case of pure indium. This cannot be assigned merely to a difference in thermal expansion in the directions of the *a* and *c* axes of the unit cell, for an actual contraction in the direction of the *c* axis is found to occur as the temperature is raised. The change appears to indicate a reduction in the asymmetry of the indium atom with increase in temperature, and a complete investigation of the phenomenon is desirable.

§ 6. CADMIUM-RICH PHASE

The phase precipitated from the indium-rich solid solution on crossing the solubility limit consists, according to Wilson and Wick, of cadmium with less than 1 per cent of indium in solution. The Debye-Scherrer photographs of the alloys containing more than 8 per cent of cadmium showed lines due to the precipitated phase, and these were all found to coincide with lines of the pattern for pure cadmium. In the photographs taken by the focusing method the reflection from the {212} planes of the cadmium lattice was recorded for these alloys, and it was measured in the case of the alloys 20.5 and 25.6; a similar photograph was taken with pure cadmium for comparison. The spacings found were: cadmium, 0.91912 ± 0.0002 Å.; alloy 20.5, 0.91926 Å.; alloy 25.6, 0.91930 Å.

Since no change greater than the probable error in measurement was detected, the precipitated phase appears to have been almost pure cadmium, in agreement with the statement of Wilson and Wick, but no limit to the amount of indium in solution can be fixed, since the variation of the $\{212\}$ spacing of the lattice with composition cannot be determined.

§ 7. DISCUSSION OF RESULTS

The determination of the solubility of cadmium in indium at 100°C . and at room temperature, which was the original object of this research, has been compared with the results obtained by microscopic methods in §§ 4, 5 and the most probable explanation of the discrepancy at room temperature has been given.

Perhaps the observation of greatest theoretical interest, however, is the transformation of the crystal structure of the indium-rich solid solution from tetragonal to cubic with increasing cadmium-content. The tetragonal nature of the lattice of pure indium has been advanced as evidence to show the incomplete state of ionization of the atoms, further evidence being afforded by the fact that the atomic diameter of the atom, determined from the closest distance of approach, is greater than would be expected from comparison with the preceding univalent element silver⁽³⁾. The present investigation has shown, however, that the asymmetry of the atom, as evidenced by the tetragonal structure, can be destroyed by the presence of about 5 per cent of cadmium without there being any change in the atomic volume. The tetragonal lattice and the large atomic diameter are not, therefore, mutually related and equally dependent on incomplete ionization.

It is very probable that a change in axial ratio similar to that observed in the present case will explain the apparent discrepancy in the constitutional diagram determined for the lead-indium system⁽⁴⁾. These two metals are stated to form an unbroken series of solid solutions, but doubt has been cast on this conclusion because of the different lattice structures of the pure metals. A gradual change from tetragonal to face-centred cubic at the indium end of the diagram would remove the difficulties

Ageew and Ageewa⁽⁵⁾ have found that the two metals do not form a continuous series of solid solutions, the structure of the indium-rich solid solution remaining tetragonal up to the phase boundary with no well-marked change in axial ratio. It is felt, however, that another examination of the system would be of value, the possibility of a transformation such as that described above being borne in mind.

§ 8. ACKNOWLEDGEMENTS

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A SIMPLE TYPE OF HELIUM CRYOSTAT

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ABSTRACT. Two simple cryostats for the temperature region of liquid helium are described; they have been found to facilitate experiments in that region greatly. The apparatus were constructed with the aim of combining the advantages of a small liquefier with those of an ordinary helium cryostat.

§ 1. INTRODUCTION

TWO different techniques have been employed hitherto in handling liquid helium. One was developed in Leiden in close resemblance to experiments with liquid air and liquid hydrogen; helium is liquefied in a standard liquefying unit, and the liquid is transferred into a Dewar vessel in which it can be carried about. The specimen under investigation and the measuring apparatus are immersed in this bath of liquid helium. The other technique, which was developed by Simon and his collaborators, employs a compound apparatus in which a small helium liquefier is directly attached to each experimental unit⁽¹⁾.

The advantage of the helium bath is the comparatively simple arrangement of the apparatus, which makes it easy to change specimens. Its disadvantages are the high price made necessary by a big liquefaction unit, the necessity of using great amounts of helium, large pumps, and so on, and the difficulty of controlling temperature. The compound apparatus on the other hand is free from these disadvantages and is especially adapted to the conditions at very low temperatures, where it is possible to carry out practically all experiments with only a very small amount of liquid helium, since the latent heat of the cooling agent is very high in comparison with the heat capacities of most substances. A disadvantage of the compound apparatus, however, is the work imposed on the researcher, who, in order to insert a new specimen, has to take the apparatus to pieces and to resolder and test one or more vacuum cases. As these cases have to hold a vacuum of 10^{-6} cm. of mercury the reassembling requires much care and time. It is further necessary to warm up the apparatus to room-temperature in order to insert a new specimen, which is very uneconomic when a great number of specimens is to be investigated.

We have developed a type of apparatus which combines the advantages of the helium bath and the compound apparatus. As two of these cryostats have now been in use for two years and have proved extremely useful for various experiments at liquid helium temperatures, a detailed description of them seems justified.

The first apparatus, A, was so designed that the specimen was kept in the liquid helium itself and could be exchanged several times, the same helium, produced in one liquefaction, being used throughout. In the second apparatus, B, the specimen can be changed between two helium liquefactions without the apparatus having to be warmed above the temperature of liquid hydrogen.

§ 2. APPARATUS A*

In order to illustrate the principle of the liquefier, a simplified diagram is given in figure 1. The helium liquefaction was carried out by the expansion method⁽²⁾ in which helium gas, compressed to a high pressure, is allowed to expand adiabatically from a low starting temperature produced by solid hydrogen.

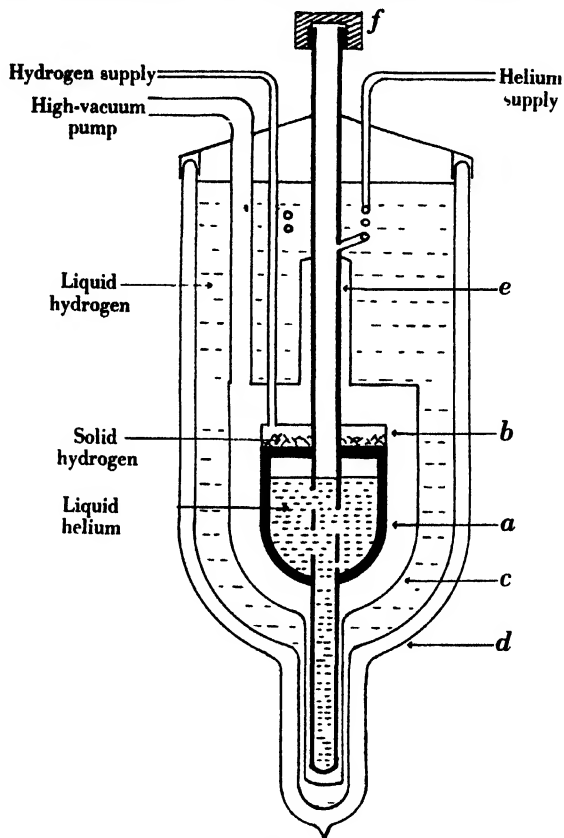


Figure 1

a represents a strong-walled high-pressure helium chamber to which the hydrogen container *b* is attached. *a* and *b* are kept in the vacuum jacket *c* which can insulate thermally the helium chamber from the liquid hydrogen in the glass Dewar

* Apparatus A was constructed with the collaboration of Dr R. B. Pontius.

vessel *d*, surrounding the whole apparatus. The helium chamber is suspended on a strong-walled tube *e*, extending to the top of the apparatus. This tube, which is of German silver, is closed at the top by a heavy nut *f* which can withstand the pressure of 150 atmospheres in the helium chamber before an expansion is made. The specimens were inserted in the helium chamber through this long tube and in the actual apparatus they were situated in a long tail-like projection of the helium

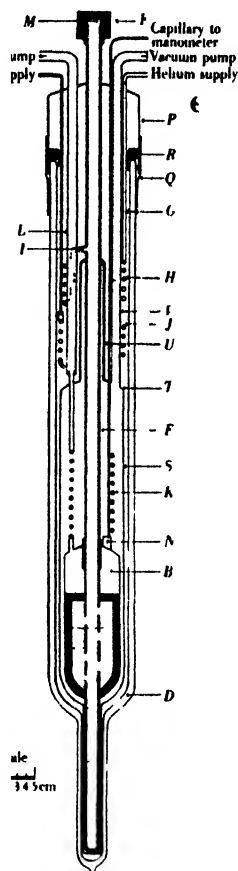


Figure 2

chamber. This shape of the lower end of the apparatus served to facilitate magnetic experiments. After the compressed helium had been expanded and liquid helium obtained in the helium chamber, the nut *f* was unscrewed and replaced by a cap which could support any electrical or mechanical connexions to the specimen. It was found quite possible with this arrangement to change specimens when liquid helium was in the apparatus, so that several different specimens could be used during one run. In no case however was it necessary in changing specimens to disturb any vacuum-jacket joints, which are always left sealed.

The temperature of the specimen was determined by measuring the vapour pressure of the surrounding liquid helium which was in actual contact with it.

A complete diagram is given in figure 2. The whole apparatus was suspended by the tube *e* from the brass cap *p*. The glass Dewar vessel *d* was joined to the cap by means of a rubber sleeve *q* with a packing of felt *r* between the metal and glass.

The vacuum jacket consists of the cylindrical copper tube *s* which is soldered with Wood's metal to the copper cap *t*. This cap is attached to the tube *e*, through the tower *u*. This tower was employed in order to increase the distance between the points at hydrogen temperature and at helium temperature along the tube *e*, in order to isolate thermally the helium chamber more effectively, without at the same time giving too large a volume to the vacuum jacket. The tower was made of thick-walled copper tubing which conducted heat well, so that towards the end of an experiment the level of liquid hydrogen could fall to the bottom of the tower while the tube *e* would continue to retain the temperature of liquid hydrogen at the place at which it enters the vacuum jacket. The vacuum jacket was shaped to surround the tail, as shown in the diagram. All the parts of the jacket were of copper, tinned on the outside to block up the porous holes which are found to exist in copper, and soldered together with Wood's metal. The exhaustion of the vacuum jacket was carried out through the thin-walled German-silver tube *v*.

High-pressure helium previously cooled in liquid air was led in through the German-silver tube *g* and passed through the copper spiral *h* immersed in the liquid hydrogen, before entering the helium chamber through the tube *e* at *i*. Hydrogen was condensed in the space *b* by allowing hydrogen gas at a small over-pressure to circulate in the copper spiral *j*. The spiral *k* was of German silver, in order to make the heat connexion between the space *b* and the hydrogen bath as bad as possible. The condensed hydrogen could be pumped off through the thin-walled German-silver tube *l*, in order to obtain solid hydrogen at about 10° K. in the space *b*. The joint on the cap *f* was sealed with a lead washer *m*. A small helium gas thermometer *n* was connected by a German-silver capillary to a dial vacuum manometer, in the manner described in detail by Mendelssohn⁽³⁾. Particulars are given in table 1.

Table 1. *Details of apparatus A*

Part	Material	Inside diameter	Outside diameter
Tube <i>e</i>	German silver	1.1 cm.	1.6 cm.
Spirals <i>h</i> and <i>j</i>	Copper	$\frac{1}{8}$ in.	$\frac{1}{4}$ in.
Spiral <i>k</i>	German silver	3.6 mm.	4 mm.

The specimens were always connected to a long glass or German-silver tube which reached up to the cap *f*. This tube also carried the electrical connexions leading to the specimen. After the helium had been liquefied by expansion and while it was boiling under atmospheric pressure,* cap *f* was unscrewed and the electrical wires leading to the specimen were taken out† through the new cap which

* As the tube *i* was connected to a gasometer the helium was actually boiling at an over-pressure of 2 cm. of mercury.

† Of course only specimens which withstood the pressure of 150 atmospheres could be inserted before the liquefaction.

was fitted instead of *f* and which contained a wide tube. This tube could be connected to a strong pump to pump off the liquid helium. Owing to the great width of *e* and this connecting tube the liquid helium could be kept boiling at temperatures as low as 1.3°K .

For different kinds of experiments different caps were employed. Figure 3 shows a cap that was employed for induction experiments. The German-silver tube

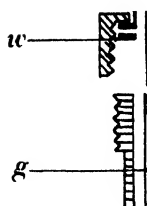
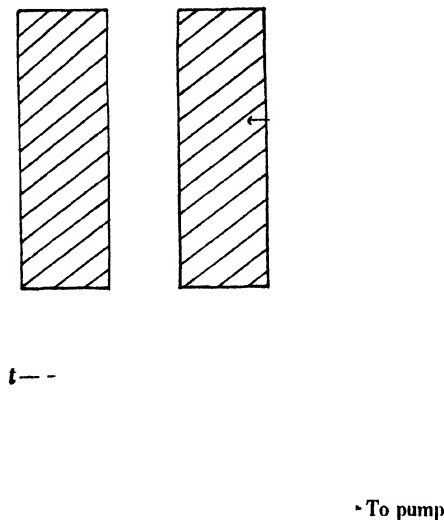


Figure 3

g, which bore the specimen at its lower end, was threaded at the upper end, and to this thread could be screwed a rod *r* which at its upper end bore a cylinder *c* of soft iron. Rod and cylinder were surrounded by the tube *t* sealed at the top and having at its lower end a flange *l*, which could be pressed on to the upper end of the tube *e* by a nut, a vacuum-tight joint being obtained by means of the washer *w*. By means of the solenoid *s* the soft-iron cylinder could be pulled up in *t*, in turn withdrawing the specimen from a search coil.

It was found that the rate of evaporation of liquid helium in this apparatus was approximately 7 cm^3 per hour. Consequently it was possible, if good conditions

of pressure and temperature had been obtained before the expansion, to keep liquid helium temperatures for twelve hours or more.

Another alternative was to make experiments of a shorter duration and to use part of the liquid helium to cool a second or a third or even a fourth specimen. The procedure for changing the specimen was the following. After the cap had been unscrewed the old specimen was withdrawn and the new one, previously cooled in liquid air, was quickly inserted into the top of the tube *e*. But before the specimen

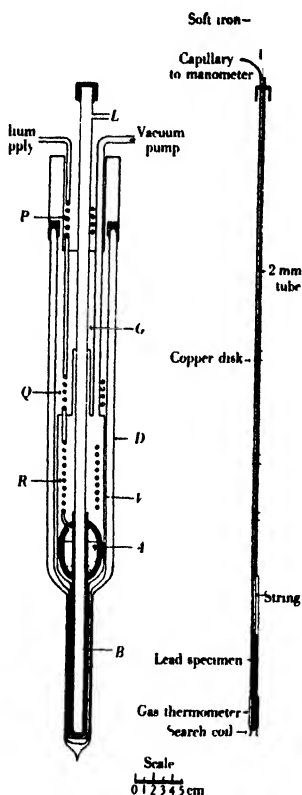


Figure 4

was allowed to reach the liquid helium it was kept for some time high up in the tube *e*, above the tower *u*, where it could take up the temperature of the surrounding hydrogen bath. The evaporating helium acted as heat-exchanging medium between the specimen and the bath. When it was certain that the specimen had reached the temperature of the boiling hydrogen, it was gently lowered into the liquid helium. In order to avoid loss of helium or condensation of air into the apparatus during the exchange of the specimens, the outlet tube *e* was covered with a temporary cap of plasticine through which the long rod bearing the specimen was withdrawn or lowered. The evaporating helium left the apparatus through the high-pressure tubes and spirals via *i* and was collected in a gasometer.

§ 3. APPARATUS B

Apparatus B, which also worked with the expansion method, was smaller than apparatus A and was employed when experiments of two hours' duration or less were carried out. It was also possible with this apparatus to make experiments in the temperature region between 4° and 10° K. A diagram is given in figure 4. The specimen was again introduced through the long German-silver tube *g*, which however did not communicate directly with the helium chamber. *g* had thin walls (0.1 mm. thick) and bore at its lower end the helium chamber *a*. Through the middle of *a* there was a strong-walled copper tube *b* which projected considerably beyond the lower end of the helium chamber and was closed at the bottom. *b* formed a continuation of *g*. The whole arrangement was suspended in the vacuum jacket *v*. Before *a* and *b* were embodied in the apparatus the whole unit was carefully annealed for twenty-four hours to ensure good heat-conduction along *b*. Helium was supplied to *a* by the tube *r* which before entering the vacuum space was coiled at *q* in order to precool the helium in liquid hydrogen. In order to minimize the evaporation of liquid hydrogen, the cap of the apparatus was constructed to form a container for liquid air, through which the tubes leading to the apparatus passed. The compressed helium entering the apparatus was precooled to the temperature of liquid air in the spiral *p*. The helium chamber had no hydrogen space attached to it as apparatus A had. As the hydrogen bath was small and the influx of heat was reduced by the liquid air in the cap, a low enough starting temperature for the expansion could be obtained by pumping the whole hydrogen bath with a good rotary pump. The temperature of *a* was indicated by a gas thermometer similar to the one in apparatus A, which was attached to the top of the helium chamber (not shown in the drawing).

Table 2. Details of apparatus B

Part	Material	Inside diameter	Outside diameter
Tail <i>b</i>	Copper	1.1 cm.	1.6 cm.
Spirals <i>p</i> and <i>q</i>	Copper	$\frac{1}{8}$ in.	$\frac{1}{8}$ in.
Spiral <i>r</i>	German silver	3 mm.	4 mm.

As the space containing the specimen was not subjected to high pressure, as it was in apparatus A, the specimen with its special cap and attachments was always inserted before the liquefaction. As an example, the arrangement which was employed to measure the induction in a lead rod is shown in figure 4*a*. The specimen can be withdrawn from the search coil by means of a string connected to a lump of iron at the top of the apparatus, which can be pulled up with a magnet. The temperature of the specimen is determined by means of a gas thermometer. Circular copper discs, which have the same diameter as the internal width of the German-silver tube *g*, prevent convection currents in the helium gas which could give an unwanted heat-exchange between the lower and upper ends of the tube. During the experiment helium gas of a few mm. of mercury was kept in the tube *g*.

To exchange a specimen for another after one liquefaction, without removing the bath of liquid hydrogen, *g* was connected through *l* to the gasometer, thus giving a slight over-pressure of helium and preventing the condensation of air in the tube. The exchange of specimens was carried out in very much the same way as that described for apparatus A.

In order to test the homogeneity of temperature along *b*, a preliminary experiment was carried out in which the bulb of a helium gas thermometer was allowed to travel up and down in *b*. It was found that the variation of temperature was less than 0.02° . The heat-influx into this apparatus was comparatively small, so that only 4.5 cm^3 of liquid helium evaporates in one hour.

When experiments between the temperature ranges of liquid helium and liquid hydrogen were to be carried out, the highly compressed gas in the helium chamber was expanded not to atmospheric pressure but only so far as to cool the apparatus to the desired temperature. Owing to the large heat-capacity of the gas remaining in the helium chamber *a*, the apparatus warmed up only very slowly; to keep the temperature constant it was only necessary to expand from time to time a little further. It was possible in this way to take readings to an accuracy of about 0.01° or less, and it was found that the same values were obtained for these temperatures when the temperature was attained by a preceding cooling or warming. This means that, with our method of keeping the temperature constant by allowing a little gas to escape from time to time, no temperature-difference of a higher order than 0.01° occurred in the apparatus.

In the temperature region of liquid helium the temperature of the cryostats could be kept constant to less than 0.003° by means of a device described by one of us⁽⁴⁾.

§ 4 CONCLUSION

The cryostats were used for a great number of various electric and magnetic experiments; a list of publications in which results obtained with these cryostats have been communicated is given at the end of the paper⁽⁵⁾. It is quite evident, however, that the cryostats can be used for other purposes also without much difficulty, for instance in optical experiments, determinations of thermal conductivities, gas absorption, and so on. The cryostats have been in constant use, sometimes twice a week, over long periods, and it was never necessary to disturb vacuum joints or any part of the liquefaction mechanism. Apart from the replacing of specimens and caps, they required no attention. They have proved especially time-saving when a series of experiments with a great number of specimens had to be carried out. As the exchange of specimens entailed practically no work, whereas in the ordinary small-scale liquefier such an exchange usually required a whole day, researches could be carried out in two or three liquefactions which otherwise would have taken several weeks.

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DISCUSSION

Dr EZER GRIFFITHS. The authors have produced an extremely compact and adaptable apparatus for work at liquid-helium temperatures.

I should like to draw attention to the gas thermometer forming part of the apparatus shown on the table. It would be interesting to know the relative volumes of the gas-thermometer bulb and the dial gauge, what precautions have to be taken to maintain the purity of the helium, and what solders and fluxes are used in the construction of the apparatus.

AUTHORS' REPLY. The ratio of the volumes of the thermometer bulb to the dial gauge is about 1 : 10. At this ratio the temperature interval between 0 and 20° K. covers roughly two-thirds of the gauge scale.

The helium coming from the compressor passes an oil strainer and a trap containing charcoal that dips into liquid air.

The solders employed at consecutive stages in the building of the apparatus are silver solder with borax as flux, soldering-tin, and Wood's alloy with Baker's fluid as flux.

INTENSITY OF γ RADIATION PRODUCED BY SLOW NEUTRONS

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ABSTRACT. Intensities of γ rays produced by absorption of slow neutrons have been measured for eleven elements. The results for thermal neutrons are used to calculate relative values of p , the probability of production of a γ -ray quantum by an absorbed neutron. In general, the values of p so found lie close to unity (which is the value assumed for cadmium). This observation is discussed in relation to the absolute magnitude of p , and it appears likely, in fact, that p is of the order of at least five in the elements investigated. Measurements have also been made of the γ -ray intensities as a function of the thickness of specimen for the elements silver, chlorine and mercury. These lead to approximate determinations of the absorption coefficients of thermal neutrons in these elements. For slow neutrons of greater than thermal energies, the γ -ray intensities have been used to obtain the relative cross sections for γ -ray production.

§ 1. INTRODUCTION

THE production of γ radiation when slow neutrons pass through certain substances has been observed and measured by many experimenters. This emission of γ rays is usually explained by supposing capture of the incident neutron into the nucleus; the energy assigned to the radiation being such that the total energy in the process is conserved. To interpret the capture process on the lines of the Bohr theory of the nucleus, we may say that the neutron and nucleus form a new intermediate nucleus, which may attain its ground state by one or more transitions. We will denote this number of transitions by p ; thus p represents the number of γ -ray quanta emitted per absorbed neutron.

The question of the magnitude of p has been investigated theoretically by Bethe and Bacher⁽¹⁾, and experimentally by Fleischmann⁽²⁾ and by Griffiths and Szilard⁽³⁾. Theory indicates that the number of γ -ray quanta is probably quite large; but whereas the latter experimenters found for cadmium a value of p greater than or equal to 7, the former obtained the value 1. Both these absolute evaluations involved difficult estimates of tube-counter efficiency and of geometrical factors. Another method of obtaining some information of the magnitude of p is to compare the values of p for various elements. For instance, if the values were to fall into a definite integral relationship with one another, it would be clear that at least for some of the elements the absolute values of p are greater than 1.

Relative measurements of p for a number of elements have already been made by Griffiths and Szilard⁽³⁾, who found that the values are reasonably constant.

The experiments to be described below determine relative values of p for eleven elements, thermal neutrons being used. For non-thermal neutrons, relative cross sections are calculated, since the information for obtaining p is unavailable.

§ 2. EXPERIMENTAL ARRANGEMENT

Figure 1 shows the arrangement of the apparatus used to investigate the emission of γ radiation. The γ radiation was detected by a tube counter, 6 cm. long and 3 cm. in diameter. The pulses were amplified and then counted by a scale-of-four counter of the type described by Wynn-Williams and Ward⁽⁴⁾. The counter was placed in a lead cylinder whose walls were 2 mm. thick, this thickness being sufficient

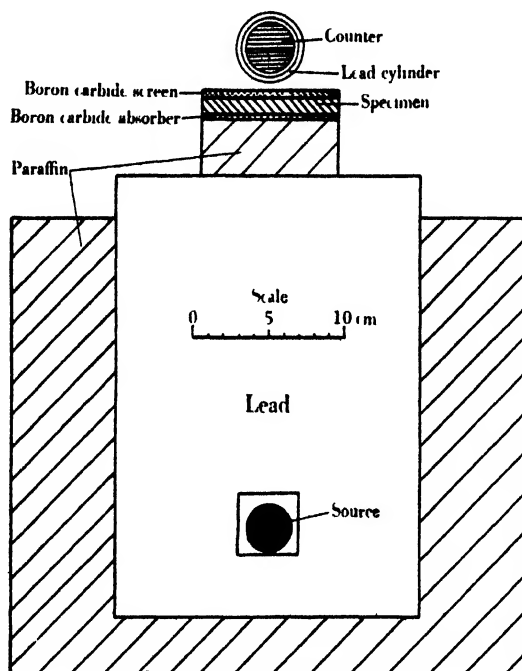


Figure 1. Experimental arrangement.

to prevent any β particles arising in the specimen from reaching the counter. The specimens in which γ radiation was induced were, in general, of rectangular cross section measuring 9×7 cm² and of sufficient thickness to produce a conveniently measurable effect. They were placed directly under the counter, and were completely covered on the top face by an absorber of boron carbide which totally absorbed the thermal neutrons scattered to the specimen from the surroundings. Absorbers of boron carbide could be placed immediately below the specimen.

Cadmium, silver, copper and iron were measured in the form of solid blocks, mercury and chlorine (as carbon tetrachloride) as liquids in a thin iron container, and arsenic, vanadium, iodine, antimony, tin in the form of powder contained in small tins.

The remainder of the arrangement comprises a quantity of paraffin to produce the necessary slow neutrons and sufficient lead between the counter and the radon-beryllium source to reduce the background count to a reasonable figure.

§ 3. MAGNITUDE OF EFFECTS

With the counter used, the normal natural count was approximately 60 per min. The count with a 350-millicurie radon-beryllium source in position was 300 per min. A cylinder of cadmium surrounding the counter then increased the count to 700 per min. This effect of 400 per min. is the largest effect measured, the minimum being about 30 per min. This is the corrected effect as described in the next section, correction being made for γ -ray absorption in the specimen. In the tables, experimental activities are given relative to either cadmium or silver. The actual effect for silver with non-thermal neutrons was about 60 per min. With the smaller effects even long periods of counting were not sufficient to give very great accuracy.

§ 4. EXPERIMENTAL METHOD

For each specimen, measurements of the γ -ray effect were made for both thermal and resonance neutrons. Measurements of the counting rate were made (1) without the specimen, (2) with the specimen in position, and (3) with the specimen in position and a filter of boron carbide between it and the source, of sufficient thickness to eliminate the thermal neutrons.

The difference between (2) and (1), after the corrections described below had been applied, gave the γ -ray activity produced by both thermal and non-thermal neutrons. The difference between (3) and (1), similarly corrected, gave the activity due to non-thermal neutrons alone.

The first and most important correction is that for absorption of γ rays from the source and surrounding paraffin in the specimen and boron-carbide filter. This correction was determined experimentally by measuring the absorption of γ rays in the various specimens when the neutron-source was replaced by one of pure radon. It is assumed that the γ rays in this case are nearly the same as those incident on the counter when a neutron-source is in position. The γ rays in the latter case differ only by the addition of some γ radiation produced by the absorption of neutrons in the paraffin, and by the presence of the hard γ radiation produced during the α -particle-beryllium reaction in the source. The latter radiation is comparatively weak, while the γ rays arising from the neutron-proton reaction have nearly the same energy as the primary γ rays from the source^(5,6). The validity of this method was confirmed by subsidiary experiments in which the absorption in lead of the radiations from the neutron and pure radon sources were compared.

The second correction was for the different effective distances of the specimens below the counter. It was determined experimentally by measuring the effect due to a sheet of cadmium placed at different distances below the counter. To apply the correction a mean distance was first calculated from the absorption coefficients of thermal neutrons as given by Dunning and his co-workers⁽⁷⁾.

§ 5. EXPERIMENTAL RESULTS

To compare the activities of the different specimens the relation

$$I = Np \frac{\mu_n}{\mu_n - \mu_\gamma} (e^{-\mu_\gamma l} - e^{-\mu_n l}) \quad \text{.....(1)}$$

has been used in the reduction of the results. Here I is the total intensity of γ rays from the upper surface of the specimen, in quanta per unit time; N is the number of neutrons, thermal or non-thermal, incident on the specimen per unit time; p is the probability of production of a γ -ray quantum by an absorbed neutron; μ_n is the mass absorption coefficient of neutrons, thermal or non-thermal, in the specimen; μ_γ is the mass absorption coefficient of induced γ rays in the specimen; and l is the mass per unit area of the specimen.

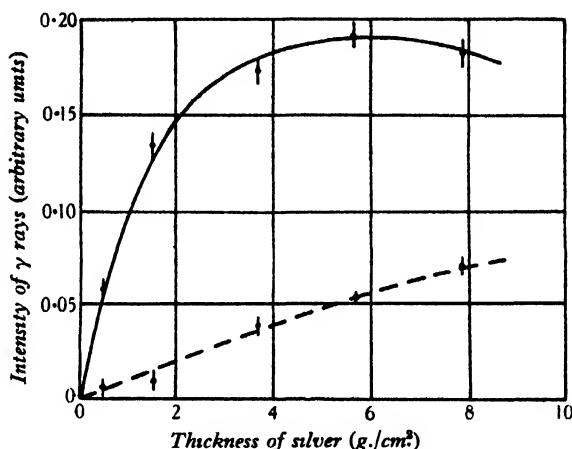


Figure 2. Excitation of γ rays in silver. — Thermal neutrons; ---- resonance neutrons.

Thermal neutrons. In previous work thermal neutrons have been separated from those of non-thermal energies by placing a sheet of cadmium of thickness nearly 0.5 mm. in the neutron beam. The neutrons so absorbed have been defined by Fermi and Amaldi as C neutrons. This method of isolating thermal neutrons is unsuitable when γ rays are being investigated, owing to the intense γ radiation from the cadmium sheet. For this reason a boron-carbide filter has been used to absorb the thermal neutrons. Boron absorbs slow neutrons strongly, but produces only a weak γ radiation.

To correlate this work with results published by other workers who used cadmium to separate thermal neutrons, it is necessary to know the absorption coefficient of thermal neutrons in boron. The mass absorption coefficient has been measured by Livingston and Hoffmann⁽⁸⁾, who obtain the value $\mu/\rho = 36 \text{ cm}^2/\text{g}$. Mitchell⁽⁹⁾ as well as Goldsmith and Rasetti⁽¹⁰⁾ give the value $\mu/\rho = 28 \text{ cm}^2/\text{g}$. All these determinations were made with detectors whose sensitivity varied inversely as the neutron-velocity. Measurements carried out by Burhop and others⁽¹¹⁾ by an entirely

independent method support the higher value of μ/ρ . Their value, $\mu/\rho = 38 \text{ cm}^2/\text{g.}$, will be used. From this, it is readily calculated that our boron-carbide filter (containing 0.0614 g./cm^2 of boron) absorbs 87 per cent of the C neutrons as detected by a v^{-1} -law detector.

The γ -ray activity as a function of the specimen-thickness has been investigated for the elements silver, chlorine, mercury. Figure 2 shows a typical curve, obtained for silver. As is indicated by equation (1), the activity I is given as a function of the thickness by the difference between two exponential terms, $\exp(-\mu_\gamma l)$ and $\exp(-\mu_n l)$, so that by assuming a value for μ_γ , a determination of μ_n can be made from the form of the curve.

The values of μ_γ for the absorption of the radiations in the specimens themselves have been calculated from the energies of the γ -ray quanta as determined by various workers^(5,6). These values are shown in column 4 of table I. The values of μ_n then determined as above, are given in column 5 and, for comparison, the values found by Dunning and co-workers and Szilard and Griffiths are included in the next columns. The present authors' values are seen to agree reasonably well with those of other workers except in the case of mercury.

Table I

Element	Thickness (g./cm ²)	Experimental activity	μ_γ calculated (cm ² /g.)	μ_n authors (cm ² /g.)	μ_n Dunning and co- workers	μ_n Griffiths and Szilard	p authors	p Griffiths and Szilard
(17) Chlorine	1.73	0.912	0.061	0.65	0.65	0.89	1.22 ± 0.16	0.95
(23) Vanadium	1.68	0.174	(0.033)	—	0.118	—	0.95 ± 0.10	—
(26) Iron	10.2	0.317	0.029	—	0.13	—	0.74 ± 0.18	—
(29) Copper	5.38	0.178	0.029	—	0.0713	—	0.60 ± 0.18	—
(33) Arsenic	3.61	0.162	0.035	—	0.070	—	0.78 ± 0.14	—
(47) Silver	5.25	0.211	0.0346	0.50	0.309	0.54	0.96 ± 0.11	0.75
(48) Cadmium	0.434	1.00	0.0340	—	15.5	24.4	1.00	1.00
(50) Tin	4.20	0.109	0.039	—	0.0204	—	1.48 ± 0.40	—
(51) Antimony	5.88	0.160	(0.04)	—	0.0403	—	0.85 ± 0.14	—
(53) Iodine	5.51	0.142	(0.04)	—	0.0448	—	0.72 ± 0.18	—
(80) Mercury	1.76	0.678	0.040	0.63	1.145	1.04	1.03 ± 0.10	1.05

In the majority of elements the γ -ray activity has only been found for one thickness of specimen. In these cases, the value of p has been calculated relatively to cadmium, for which p has been taken arbitrarily as 1. For this purpose a knowledge of both μ_γ and μ_n is necessary; μ_γ is obtained as described above, while μ_n is taken from Dunning's results. The resulting values of p are tabulated in column 8, while some values obtained by Griffiths and Szilard are given in column 9.

As can be seen from the table, the values of p lie reasonably close to unity. This observation may be interpreted in either of two ways. The departures from unity may be attributed to experimental error and the results taken as indicating that the values of p are the same for all elements. If this be the case, then, the simplest hypothesis to make is that the nucleus following the capture of the neutron reaches the ground state in a single transition. On the other hand, if the departures are considered as real the results indicate the existence of rather large values of p which are all of much the same order of magnitude for the elements here studied.

In this case, we may conclude that the average number of γ -ray quanta emitted per absorbed neutron is at least five. This conclusion is consistent with the observations of Griffiths and Szilard for cadmium and has the theoretical support of Bethe and Bacher.

Non-thermal neutrons. The γ -ray activity produced by non-thermal neutrons has been studied as a function of thickness for the element silver. The results are graphed in figure 2. In table 2 the experimental activities for single thicknesses of

Table 2

Element	Thickness (g/cm ²)	Experimental activity	σ_γ relative to A
(26) Iron	10.2	0.70 \pm 0.25	0.13 \pm 0.05
(29) Copper	5.72	0.83 \pm 0.25	0.32 \pm 0.10
(33) Arsenic	3.61	0.36 \pm 0.13	0.26 \pm 0.09
(47) Silver	3.68	1.00 \pm 0.16	1.00 \pm 0.16
(51) Antimony	5.88	0.46 \pm 0.13	0.32 \pm 0.09
(53) Iodine	5.51	0.76 \pm 0.19	0.59 \pm 0.15
(80) Mercury	20.7	1.59 \pm 0.32	0.52 \pm 0.11

six elements relative to silver are shown and the corresponding relative cross sections tabulated. These cross sections have been calculated from the relation

$$\sigma_\gamma = \frac{IA}{l},$$

where σ_γ is the relative cross section, I the intensity of the γ rays, A the atomic weight of the specimen, and l the superficial mass of the specimen. The value of σ_γ is then reduced so as to make the cross section for silver unity. The use of the above relation is justified, since the experimental activities have been corrected for γ -ray absorption in the specimen.

§ 6 ACKNOWLEDGEMENTS

We take this opportunity of thanking Dr E. H. S. Burhop for his advice and help with the investigation. We are also indebted to the Commonwealth X-ray and Radium Laboratory for supplying us with the necessary radon to perform the experiment. Both authors were aided by research grants from the University of Melbourne.

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THE MOTION OF A MERCURY INDEX IN A CAPILLARY TUBE

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ABSTRACT. The general case of the motion of an index of any liquid is considered theoretically and it is shown that the viscosity of the liquid can be determined by observation of the velocity of the index when different pressure-differences are applied between its ends. Experiments on the motion of mercury indexes are described; they lead to a value of the viscosity which is about 6 per cent higher than the accepted value. The discrepancy is attributed to the electrification of the walls of the tube which continues to increase slowly even after the index has made several excursions along it. It is found that the difference between the angles of contact at the two ends is practically independent of the velocity of the index.

§ 1. INTRODUCTION

IT was shown many years ago by Jamin⁽¹⁾ that a liquid index in a tube is able to withstand quite a considerable difference in pressure between its ends without being caused to move along the tube. Jamin pointed out that the index adjusts itself so that the two end surfaces have different curvatures, and the angle of contact between the liquid and the wall of the tube is different at the two ends. The maximum pressure-difference which the index can withstand without moving was found to be independent of its length. When the index moves along the tube the end surfaces still have different curvatures but, so far as can be ascertained, the motion was not studied by Jamin.

More recently, the motion of a mercury index in a comparatively wide tube was investigated by Rankine⁽²⁾ in connexion with his determination of the viscosities of the rare gases. In his experiments a short mercury index fell slowly in a vertical tube, driving the gas through a fine capillary tube. Rankine noted that the difference in curvature between the top and bottom surfaces causes a small reduction in the effective weight of the index, but he found the apparent reduction in weight to be independent of the length and velocity of the index. As will appear later, this is true only when the viscous forces within the index are negligible, and would not be true in a narrow tube.

The need for a more complete investigation of the motion of an index was suggested to the writer by some chance observations made with a Wilson capillary electrometer which was in use in the laboratory.

§ 2. MOTION OF AN INDEX OF ANY LIQUID

Let us consider an index of any liquid at rest in a horizontal tube which is sufficiently narrow for the end surfaces to be regarded as spherical, figure 1. Let the pressure of air in the tube be atmospheric at the right-hand end and greater than atmospheric by an amount p at the left-hand end. There is thus a tendency for the index to move from left to right, and the end surfaces adjust themselves as shown in the figure. Let us suppose that the angle of contact becomes θ_1 at the left-hand end and θ_2 at the right-hand end of the index. Then, if the surface tension of the liquid is denoted by T and the radius of the tube by a , the force opposing the pressure-difference p and keeping the index at rest is given by

$$2\pi a T (\cos \theta_1 - \cos \theta_2) = \pi a^2 p$$

and thus

$$p = \frac{2T}{a} (\cos \theta_1 - \cos \theta_2) \quad \dots\dots(1).$$

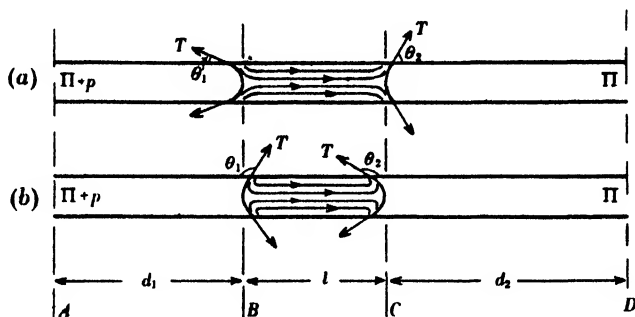


Figure 1. (a) Index of a liquid which wets the tube; (b) index of a liquid which does not wet the tube

The maximum difference in pressure which the index can withstand without moving increases as the radius of the tube is diminished, and is ultimately governed by the extent to which the angle of contact can change without the occurrence of slip. When a liquid rests in contact with a solid surface and the angle of contact has its normal value θ , the following relation holds between the surface tension T of the liquid and the tensions T_{SA} and T_{SL} of the interfaces separating respectively the solid from the air and the solid from the liquid:

$$T \cos \theta = T_{SA} - T_{SL} \quad \dots\dots(2).$$

If the angle of contact departs from the normal value, then, for equilibrium, it is necessary to suppose that there is a frictional force⁽³⁾ equal to F per unit length of the line of contact and acting at right angles to it, so as to oppose the motion of the liquid over the solid surface. Thus at one end we have

$$T \cos \theta_1 = T_{SA} - T_{SL} + F \quad \dots\dots(3)$$

and at the other

$$T \cos \theta_2 = T_{SA} - T_{SL} - F \quad \dots\dots(4).$$

Subtracting, we obtain

$$T (\cos \theta_1 - \cos \theta_2) = 2F \quad \dots\dots(5)$$

and thus

$$p = \frac{4F}{a}.$$

It is now seen that the maximum pressure-difference which the index can withstand depends on the limiting value of the friction F . In the case of most liquids the limiting friction varies widely, and in any case it depends on the state of both the solid and liquid surfaces.

When the pressure-difference between the ends becomes sufficiently great the limiting friction is exceeded and the index moves along the tube. The two end surfaces still have different curvatures, from which it follows that the frictional force F still acts when the liquid is in motion. It must not, however, be assumed that when the index is in motion F is either equal to the limiting friction or independent of the velocity of the index.

If a pool of mercury moving on a gently sloping plane surface is observed it appears to roll. The velocity of the top surface, as is shown by the movement of dust particles, is considerably greater than the velocity of the pool as a whole, while there is little doubt that the bottom surface of the mercury in contact with the solid is very nearly at rest. Similarly, when a liquid index moves in a tube it actually flows. The liquid in contact with the walls is at rest, or very nearly so, while on the axis the velocity of the liquid is greater than the velocity of the index as a whole. There is thus relative motion between the different layers of the liquid, and viscous forces opposing the motion are brought into play.

Let us now consider the flow of an index with uniform velocity in a tube of uniform bore. In the central part of the index, provided this is sufficiently long compared with the radius of the tube, it may be assumed that the motion approximates to the ordinary case of streamline flow in an infinite tube, to which Poiseuille's law applied. In this region the streamlines are parallel to the axis of the tube. Near the ends of the index, however, the streamlines cannot be parallel to the axis and it is reasonable to assume that the flow is somewhat as indicated in figure 1. Moreover, at the rear end of the index the liquid is being accelerated to the velocities characteristic of the Poiseuille distribution, while at the front end the liquid is decelerated. The kinetic energy of the index as a whole remains constant and, any dissipation of energy by turbulence being neglected, it will be supposed that the forces necessary to accelerate the liquid at the rear end are equal and opposite to the forces causing the deceleration at the front end. Thus, in the application of Poiseuille's equation, no correction will be made for the kinetic energy given to the liquid, but an end correction will be added to the length of the index to allow for the curvature of the streamlines near the ends.

The total pressure-difference between the ends of the tube when the index is in motion is now seen to be made up of three parts, (1) the term $(\cos \theta_1 - \cos \theta_2) 2T/a$ arising on account of the difference in curvature between the two ends; (2) a pressure-difference due to the viscous forces brought into play by the relative motion of the different layers of liquid; and (3) the pressure-difference required to drive air along the sections AB and CD of the tube.

Poiseuille's equation for an incompressible fluid may be written in the form

$$p_1 - p_2 = \frac{8\eta l V}{\pi a^4},$$

where the symbols have their usual significance. The effective length of the index which must be used in calculating term (2) in the preceding paragraph is greater than the actual length l and may be taken as $(l+x)$, where x , the end correction, is some function of the radius of the tube. If v is the velocity of the index as a whole, the volume of liquid passing any cross-section of the tube per second is $\pi a^2 v$ and thus, in order to maintain the flow, there must be a pressure-difference $8\eta v (l+x)/a^2$.

Since the viscosity η' of air is small compared with the viscosity η of the liquid, and since the actual mean pressures of the air in the sections AB and CD of the tube, figure 1, are large compared with the pressure-difference p , we may use the same form of Poiseuille's equation for the flow of the air as for the flow of the liquid. Thus for the fall in pressure along the section AB of length d_1 we have $8\eta' v d_1/a^2$, and for the fall in pressure along the section CD of length d_2 we have $8\eta' v d_2/a^2$, an end correction being unnecessary in this case. If the total length of the tube is L these two pressure-differences may together be represented by the term $8\eta' v (L-l)/a^2$, which remains constant as the index moves along the tube. For the total pressure-difference between the ends of the tube we now have the expression

$$p = \frac{8v}{a^2} [(l+x)\eta + (L-l)\eta'] + \frac{2T}{a} (\cos \theta_1 - \cos \theta_2) \quad \dots\dots(6).$$

It had been hoped that a method might be developed by which the viscosity of a small volume of a liquid might be determined by measurement of the velocities of indexes of different lengths with different values of the driving pressure p . However, in the case of liquids which wet the tube, it was found that the film of liquid left behind on the walls, which is inherently unstable, very quickly collects together to form a number of small indexes which complicate the motion. Experiments have in consequence only been made with mercury indexes, and these experiments will now be described.

§ 3. EXPERIMENTAL PROCEDURE

Some difficulty was experienced in obtaining uniform glass capillary tubes sufficiently long to enable accurate measurements of the velocity of the index to be made. Eventually, three soft-glass tubes were selected, each of length 150 cm.; their cross-sectional areas, as determined by measurement of a mercury index, did not vary by more than 2 per cent from the mean value. The mean radii of the tubes found from the weight of mercury required to fill them were respectively 0.0277, 0.0503 and 0.1014 cm. The tubes were mounted side by side on wooden supports screwed to the bench and adjusted so as to be accurately horizontal, their ends being bent as shown in figure 2 to facilitate the introduction at A and removal at B of the mercury indexes. Each end of each tube could be either opened to the atmosphere or connected to the reservoir C in which the pressure was raised

above atmospheric. The reservoir was of about 6 litres capacity and contained calcium chloride. The manometer *D* contained xylene, of specific gravity 0.866. Each tube was carefully washed and dried before use, and only clean redistilled mercury prepared by Hulett's⁽⁴⁾ method was used for the indexes.

In order to drive the index from left to right the stopcocks T_1 and T_3 were closed and T_2 and T_4 left open. To drive the index from right to left T_1 and T_3 were opened and T_2 and T_4 closed. With this arrangement an index could be driven backwards and forwards along the tube several times while the pressure of the air in the reservoir remained sensibly constant. The terminal velocity of the index corresponding to any particular difference in pressure between its ends was obtained by timing it in both directions with an accurate stopwatch, reading to one tenth of a second, over a distance of 80 cm. in the middle of the tube. The method of timing did not introduce any systematic error.

When an index was driven along a tube which had not been used for some time, it was found that the velocity acquired under any particular pressure-difference

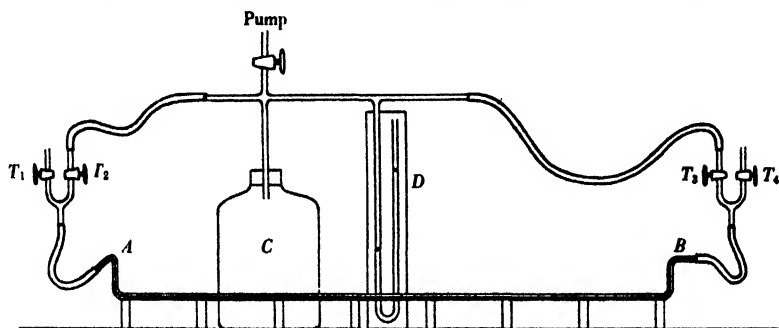


Figure 2. Arrangement of apparatus (only one of the three capillary tubes is shown).

was less than on subsequent occasions when the index had already made several excursions along the tube. This is thought to be due to the fact that during the motion of the index the mercury and glass become oppositely charged. However, after several excursions the electrification of the tube remains practically constant and only increases slowly as the index continues to move to and fro. Thus, after several excursions very little work is done in separating the charges. For this reason an index was always driven backwards and forwards along the tube several times before its velocity was recorded.

Velocities greater than about 20 cm./sec. could not be measured with sufficient accuracy on account of the difficulties of timing, while at very low velocities the indexes were found to stick. The results obtained in the range in which accurate observations of the velocity are possible are shown by the curves in figures 3, 4 and 5, which refer respectively to capillary tubes of small, medium and large diameters. Each curve represents the variation of pressure-difference with velocity for an index of the length shown. The ordinates represent the pressure-difference in cm. of xylene, and the abscissae velocities in cm./sec. Figures 3, 4 and 5 are all drawn on the same scale to facilitate comparison of the results for the different tubes.

§4. DISCUSSION OF RESULTS

It will be seen that in each case the pressure-difference necessary to drive a particular index increases linearly with increase of velocity except when the

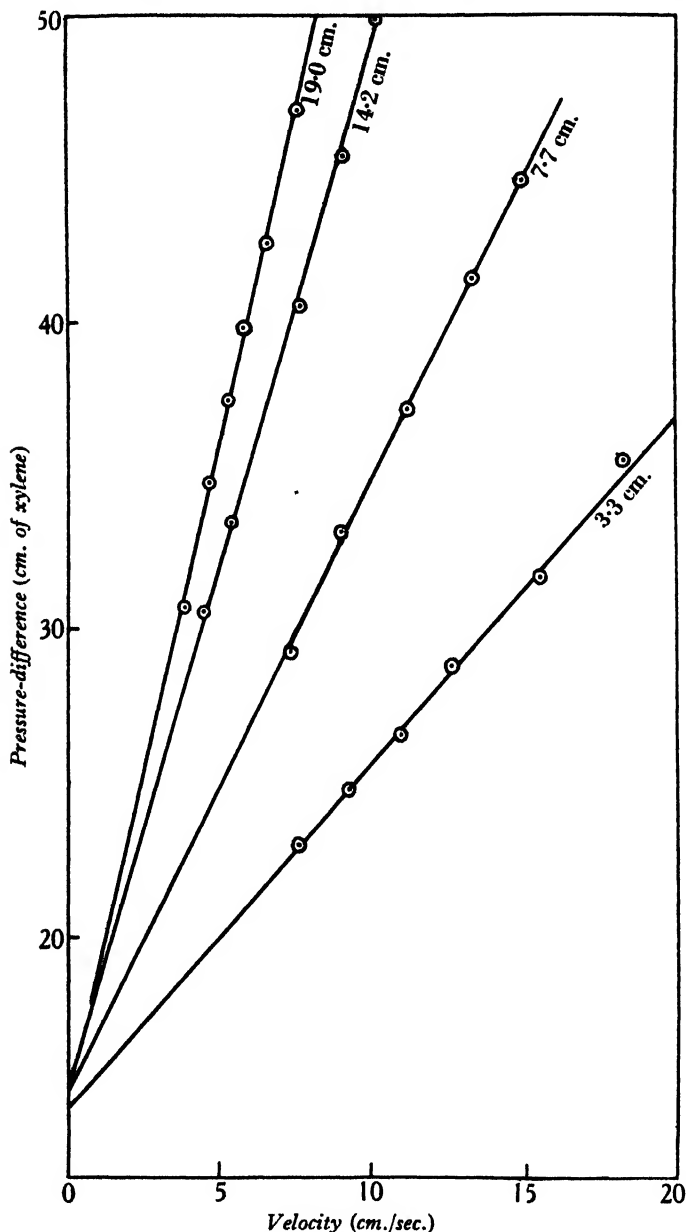


Figure 3. The variation of pressure-difference with velocity for indexes of various lengths in the tube of radius 0.0277 cm.

critical velocity is exceeded. The critical velocities for the three tubes calculated from Reynolds's formula, with the value 0.0160 g./cm.-sec. for the viscosity of

mercury at 15° C., are given in the second column of the table. The critical velocity is exceeded only in the experiments with the widest tube and, as would be expected, the rate of increase of pressure becomes more rapid beyond this point. With each tube the slope of the straight portion of the curve increases as the length of the index is increased. The slopes of the curves for indexes of similar lengths in different tubes increase as the radius of the tube is diminished.

Table 1

Radius of tube (cm.)	Critical velocity (cm./sec.)	Mean intercept (cm. of xylene)	($\cos \theta_1 - \cos \theta_2$) at zero velocity	η (g./cm.-sec.)	$\left(\frac{8\eta}{a} x + 2TB\right)$
0.0277	42.5	14.8	0.32	0.0171	2.1
0.0503	23.4	8.9	0.35	0.0169	3.4
0.1014	11.6	4.7	0.37	0.0173	11.7

Moreover, the curves in each figure all make approximately the same intercept on the pressure axis, and it is seen that the intercepts increase as the radius of the tube decreases. The intercept represents the value of the pressure-difference when the velocity of the index is zero. The mean values of the intercepts for the three tubes are given in the third column of the table. The values of ($\cos \theta_1 - \cos \theta_2$) calculated from the intercepts taking T as 547 dyne/cm. are given in the fourth column and are seen to be roughly the same for each tube. The slight increase in ($\cos \theta_1 - \cos \theta_2$) as the radius of the tube increases is probably fortuitous. Since, however, the total pressure-difference between the ends of the index increases linearly with the velocity it is clear that the quantity ($\cos \theta_1 - \cos \theta_2$) is either independent of the velocity or itself increases linearly with increase of velocity. We may represent the possible variation of the angles of contact with increase of velocity by writing

$$(\cos \theta_1 - \cos \theta_2) = A + Bv,$$

where A and B are constants. From the table it is seen that the value of A is roughly 0.35.

By differentiation of equation (6) we now obtain for the slope of each curve

$$\left(\frac{dp}{dv}\right)_{l \text{ const.}} = \frac{8}{a^2} [(l+x)\eta + (L-l)\eta'] + \frac{2TB}{a} \quad \dots\dots(7).$$

The slopes of the experimental curves for indexes of different lengths are shown in figure 6, where the three curves refer respectively to the three tubes. The points lie quite accurately on straight lines, the slopes of which are given by

$$\frac{d}{dl} \left(\frac{dp}{dv}\right) = \frac{8}{a^2} (\eta - \eta').$$

The values of η calculated from the slopes of the curves in figure 6 are shown in the fifth column of the table.

Comparison with the accepted value 0.0160 g./cm.-sec. of the viscosity of mercury at 15° C. shows the experimental values to be too high by about 6 per cent. The

errors of observation are not considered to be large enough to account for the difference, more particularly since the values of η obtained with the three tubes are consistent to within 2 per cent.

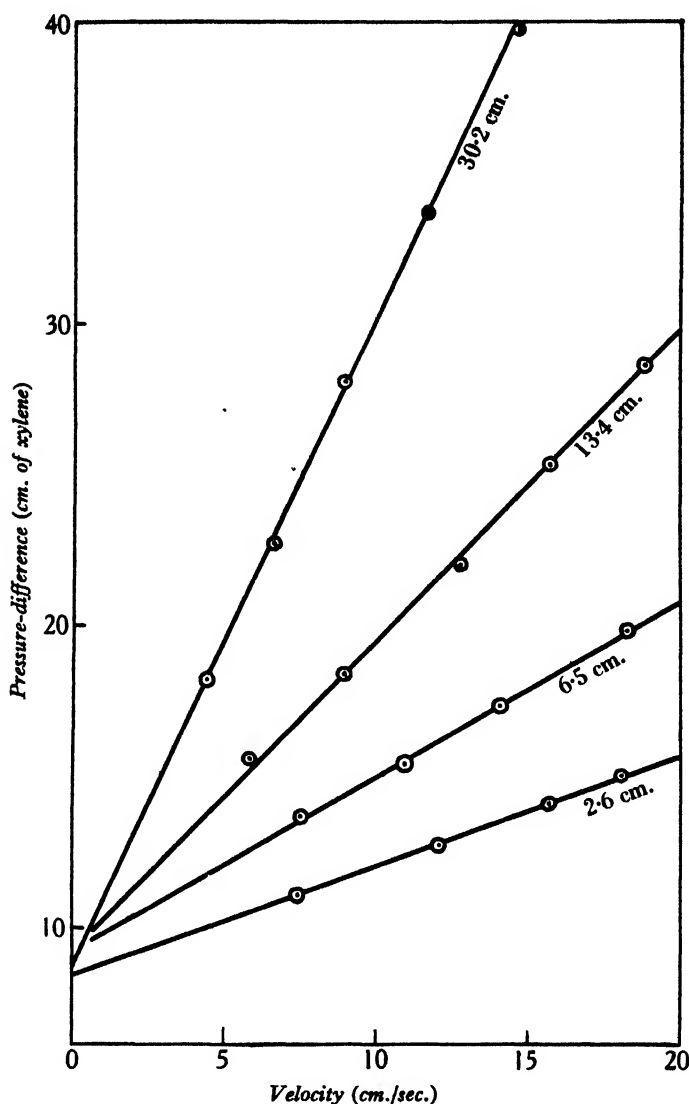


Figure 4. The variation of pressure-difference with velocity for indexes of various lengths in the tube of radius 0.0503 cm.

It seems probable that the discrepancy is due to the fact that work is always done in producing the small increase in the electrification each time the index traverses the tube. If the tube were of quartz it is likely that the electrification would become quite constant after several excursions of the index and that a more

accurate value of the viscosity would be obtained. Experiments are being made to test this view.

Nevertheless, the mere fact of electrification suggests also that the outer layer of mercury may slide over the glass and that there may be a thin film of air between the mercury and the wall of the tube. The effect of such a layer in the case of the measurement of the viscosity of mercury by the usual capillary-tube method has been discussed by Erk⁽⁵⁾ and Reiner⁽⁶⁾. Erk considers that a film of air would be quickly swept away unless it was adsorbed on the surface of the glass, in which case its effect would merely be to decrease the radius of the tube. It is generally

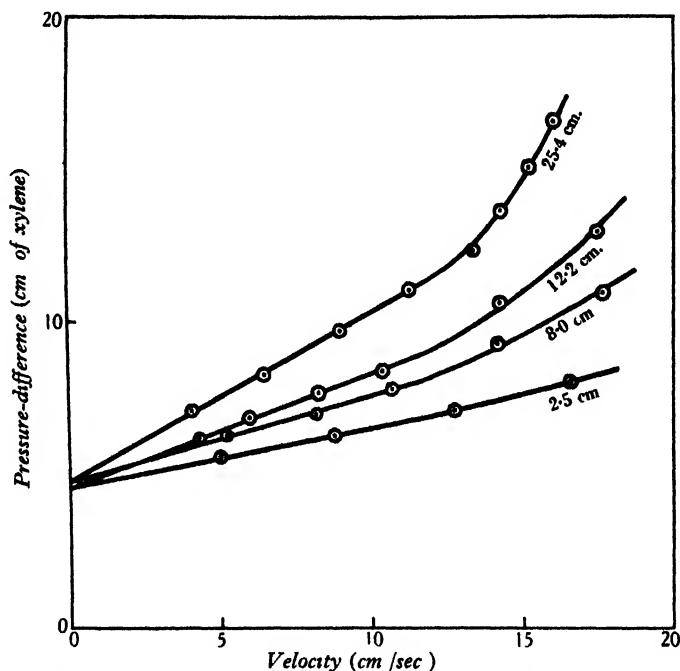


Figure 5. The variation of pressure-difference with velocity for indexes of various lengths in the tube of radius 0.1014

agreed that the effect of an adsorbed film would be too small to be detected except in extremely narrow tubes. However in these experiments, in which the moving mercury is in contact with air at both ends, it is perhaps conceivable that a layer thicker than the adsorbed layer might exist between the mercury and the glass without being swept away. The presence of such a layer would cause the measured value of η to be low. Clearly, if this error exists it is masked by the error due to the work done in electrification.

It may be urged that the error is in part due to the fact that Poiseuille's equation has been used without any allowance for the kinetic energy given to the liquid. This would be a justifiable criticism if the value of η were derived from observation of a single index. That the correction is in any case small is evident from the fact that the experimental points lie accurately on the straight lines of figures 3, 4 and 5.

Schiller and Kirsten⁽⁷⁾ have obtained a series of kinetic-energy corrections for the case of flow into a tube with a bell mouth; unfortunately, however, these corrections are not applicable to the experiments described here, and attempts to use them produced results of no value. With any one tube any kinetic-energy correction, if it were necessary, would be the same for indices of different lengths moving with the same velocity. It follows that the slopes of the curves in figure 6 would be unchanged by making the correction and the same value of η would be obtained.

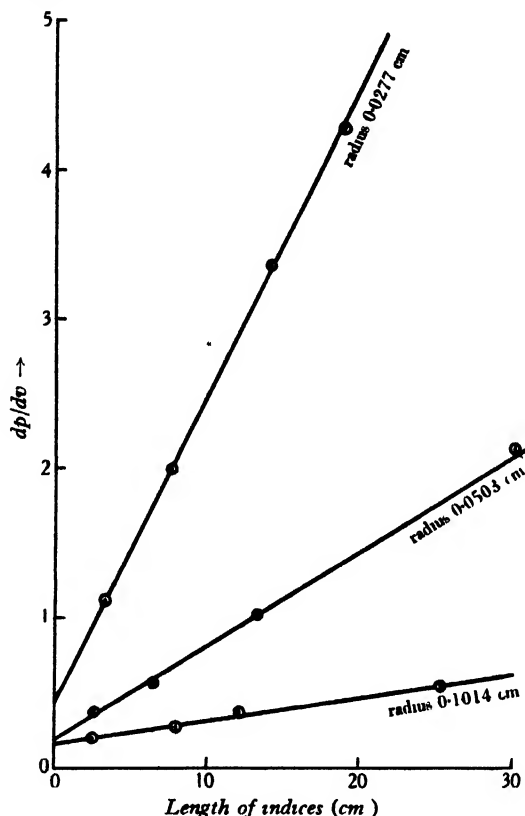


Figure 6. The variation of (dp/dv) with the length of the index for the three tubes.

We must now return to consider the possible effect of change of velocity on the angles of contact at the two ends of the index. The curves in figure 6 do not pass through the origin but make intercepts on the axis of (dp/dv) . The intercepts, denoted by Y , are obtained by putting l equal to 0 in equation (7). Thus

$$Y = \left(\frac{dp}{dv} \right)_{l=0} = \frac{8}{a^2} (x\eta + L\eta') + \frac{2TB}{a}.$$

From this equation neither x nor B can be determined separately. However it may be written in the form

$$a \left(Y - \frac{8L\eta'}{a^2} \right) = \frac{8\eta}{a} x + 2TB$$

and the quantity on the right-hand side can be calculated. The values obtained are given in the last column of the table. Although this quantity can be determined only very roughly, it clearly increases as the radius of the tube increases. It is hardly likely that B is a function of the radius and we can only suppose that the end correction α depends on some higher power of the radius. It then follows that the second term of the expression, namely $2TB$, is certainly less than $2 \cdot 1$, which means that B is less than $0 \cdot 001$. We may therefore conclude that the angles of contact at the two ends of the index are independent of the velocity throughout the range of the observations, and that the term $(\cos \theta_1 - \cos \theta_2)$ is constant and equal approximately to $0 \cdot 35$. It will be remembered that Ablett⁽⁸⁾ found that the angle of contact between water and a paraffin wax surface was independent of velocity except at very small velocities.

The actual values of θ_1 and θ_2 can now be determined. From equations (2) and (3) we obtain

$$T(\cos \theta_1 - \cos \theta) = F,$$

and from equations (2) and (4)

$$T(\cos \theta - \cos \theta_2) = F.$$

Thus by equation (5)

$$\frac{F}{T} = (\cos \theta_1 - \cos \theta) = (\cos \theta - \cos \theta_2) = \frac{1}{2} (\cos \theta_1 - \cos \theta_2) = 0 \cdot 175.$$

If we take the normal angle of contact of mercury with respect to glass as 140° , it then follows that while the index is in motion the angle of contact θ_1 at the rear end is approximately 160° , and the angle of contact θ_2 at the front end is approximately 126° .

The corresponding value of the frictional force F , which acts at the ends of the index, in opposition to the motion of the mercury over the glass surface, is found to be approximately 96 dyne/cm. It is frequently found that the difference in pressure which is sufficient to drive a short index with a small velocity is not sufficient to start the index moving from its position of rest. It must therefore be concluded that the limiting value of the frictional force is usually somewhat greater than the value of the dynamical friction given above.

An investigation of the electrification of the tube is at present in progress and the effect both of degassing the tube and of substituting a quartz tube for a glass one will be tried.

§ 5. ACKNOWLEDGEMENTS

In conclusion I should like to thank Prof. L. F. Bates and Mr N. Davy for their interest in the work.

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DISCUSSION

Dr G. D. WEST. I should like to call the author's attention to a paper by me "On the Resistance to the Motion of a Thread of Mercury in a Glass Tube" published in the *Proc. Roy. Soc.* **86**, 20 (1911). A very similar formula was there worked out (except that end corrections and the viscosity of the air were neglected), and the experimental procedure was not very different. Dr Yarnold's work, however, is clearly more accurate than my own done twenty-seven years ago, and many points are considered in much greater detail by him. I note also how much more uniform in diameter are his glass tubes. Rather striking, however, is the different value obtained for $(\cos \theta_1 - \cos \theta_2)$. My own value was some 30 per cent higher. It is possible that Dr Yarnold used cleaner mercury, or that the difference is accounted for by the use of different glass, or by a different condition of the glass surface. The suggested experiments with a quartz tube may throw some light on this matter. In fact the variations of $(\cos \theta_1 - \cos \theta_2)$ for different surfaces in contact with the mercury is a subject that the author might think worth investigation.

Professor L. F. BATES. Some time ago Dr C. J. Smith suggested that a neat modification of the Quincke method of measuring the magnetic susceptibilities of liquids might be practicable if one made use of the device invented by Professor Ferguson for measuring the surface tension of small quantities of liquid. Accordingly, Mr J. Deller made experiments in my laboratory with this object in view. He used a capillary tube, with one end ground flat, containing a strong solution of manganese sulphate of appreciable magnetic susceptibility. The tube was mounted with the ground end between poles of an electromagnet. The only magnet available at the time was of a lecture-room pattern and not powerful, and the magnetic force upon the column of liquid was not great. The motion of the column of liquid was observed on exciting the magnet, and the column was restored to its original position in several different ways, for instance by tilting the tube, by reducing the pressure on the curved surface of the column, and so on. The measurements of magnetic force thus obtained were most unsatisfactory. They were equally unsatisfactory when the experiments were repeated with the curved surface of the liquid column within the pole-gap. The method failed because the free surface was always deformed before the column moved. The experiments which the author has just described throw much light upon Mr Deller's work, for they show the enormous importance of this deformation of the surface before and during motion, and it is clear that, even if Mr Deller had used a much stronger field, reliable results could not have been obtained with this modification of the Quincke method.

Dr E. G. RICHARDSON. I wonder whether the lines of flow in a water index could be investigated experimentally, in a somewhat wider tube; this might show whether energy was being expended in eddies within the index. I doubt whether any effect due to electrification will be found. I cannot recall any authenticated effect of electrification on viscosity. The wings of birds often acquire a static charge in flight, presumably as a result of friction; and I remember some experiments being done in the Aeronautics Laboratory at Queen Mary College to test whether

an aerofoil charged to a high potential experiences a lessened resistance to an air current. The result was negative.

Dr L. HARTSHORN. I am very interested in the author's deduction of a frictional force between the mercury and the walls of the tube, which is independent of velocity. Experiments on the damping of mechanical vibrations in solid bodies and on the dissipation of energy in dielectrics in alternating electric fields also appear to demand for their explanation a force of this character, i.e. a force of the nature of soled friction rather than one of viscosity. Has the author any conception of the mechanism of such a force?

In connexion with the problem of the electrification of the tube, it might be worth while to use lead glass as this usually has a much higher electrical resistance than soda glass.

AUTHOR'S REPLY. In reply to Dr G. D. West: I am much obliged to Dr West for drawing my attention to his own work on a similar topic, which had, unfortunately, escaped my notice. I am particularly interested in Dr West's observation that the value of $(\cos \theta_1 - \cos \theta_2)$ deduced from the results of his experiments is some 30 per cent higher than the value I have given. The observations recorded in figures 3, 4 and 5 of my paper were all made with indexes freshly inserted in the tubes, but it was noticed that after an index had remained for 24 hours or more in a tube which was open to the atmosphere the pressure-difference necessary to drive it with a particular velocity was greater than it had been at first. The slope of the curve connecting pressure-difference and velocity was not appreciably different, but the intercept on the pressure axis was always greater than it had been when the index was freshly inserted. This suggests that $(\cos \theta_1 - \cos \theta_2)$ is increased by slight contamination of the mercury, which may be the cause of the discrepancy pointed out by Dr West. On the other hand, I agree with him that the nature of the glass must also affect the value of $(\cos \theta_1 - \cos \theta_2)$.

In reply to Dr E. G. Richardson: It would certainly appear to be worth while to investigate the lines of flow of the liquid in the index as suggested by Dr Richardson. I do not wish to suggest, however, that the viscosity of the mercury is any different from the normal viscosity on account of the electrification, but rather that, in so far as my method of measurement involves the performance of work against electrical forces, the value obtained for the viscosity should be greater than the true value. It does not by any means follow that the measurement of the viscosity of mercury by any of the usual viscometers, in which the liquid always fills the capillary tube, is similarly vitiated.

In reply to Dr L. Hartshorn: The suggestion that there may be some connexion between the frictional forces acting on a mercury index in a glass tube and the dissipation of energy in a dielectric is extremely interesting. I am afraid I have no conception, however, of the nature of the forces; in fact speculation seems premature until the mechanism of the normal angle of contact of a liquid is better understood.

THE PROPAGATION OF SUPERSONICS IN CAPILLARY TUBES

By J. MAY, M.Sc., King's College, Newcastle-on-Tyne

Communicated by Dr E. G. Richardson, 8 December 1937. Read 8 April 1938

ABSTRACT. The velocity and attenuation constants for the propagation of supersonic vibrations, of frequencies 40 to 115 kc./sec., in air contained in narrow tubes, of diameters 0.06 to 0.15 cm., are measured, the sources being monel needles in magnetostrictive oscillation. On comparison with Kirchhoff's theory, the results show that the absorption in the tubes is considerably greater in practice than in theory, though not markedly different from that observed at low frequencies.

§ 1. INTRODUCTION

MEASUREMENTS of the velocity and coefficient of absorption of sound in tubes have in the past been almost entirely confined to tubes of moderate areas of cross-section, in which the layer affected by viscosity can only be a small fraction of the radius. Although a considerable amount of work has been done on tubes several millimetres in diameter, one can mention only two cases in which the authors have made investigations with capillaries. The papers referred to are those by Richardson⁽¹⁾ and Penman and Richardson⁽²⁾. In the former case the author used a rubber tube 1.7 mm. in diameter and frequencies from 390 to 940 c./sec. Under these conditions he expected to have the main body of air moving under viscous resistance; he measured the amplitude at the end of the tube, using a heated platinum grid. By using a constant amplitude of air-vibration at the beginning of the tube, and by altering the length of the latter, he was enabled to plot amplitude against distance from source; thus he obtained a measure of the absorption involved.

In the second paper the authors investigated the propagation of audible sound in tubes 0.2 mm. in radius. They used a wide pipe stopped at one end firstly with teak and secondly with a bundle of tubes of the diameter quoted, and they measured the amplitude of vibration of the air in each case. They thus obtained a value for the absorption coefficient of the sound in the narrow tubes. The results in both researches gave values for absorption in excess of the value calculated by theory.

The object of the present research is to examine the propagation of sound in tubes having diameters from 1 mm. downwards at high frequencies, so that we may compare the results obtained with those already mentioned. In such cases viscosity effects may be expected to play an important part, and pertinent theories have been evolved by Helmholtz, Kirchhoff, and the late Lord Rayleigh⁽³⁾. Their

of the rod under test. *E* is an exciting coil consisting of a few hundred turns of thin copper wire wound on a paper girdle round the tube. When the rod is replaced and the rotor of the variable condenser is turned round slowly, the grid current changes in the manner described by Vincent. As suggested by Pierce, telephone receivers were used to detect the production of rod vibrations. Both a permanent magnet and an electromagnet were used successfully to provide the polarizing field. By using tubes with walls of different thicknesses it was observed that maximum oscillation of the rod was produced with narrow-walled tubes. This would be expected, since in such a case a larger percentage of the available flux permeates the rod itself.

Since thin-walled capillary tubes were unobtainable, and very narrow rods are poor vibrators, composite glass tubes were used as shown in figure 2; the

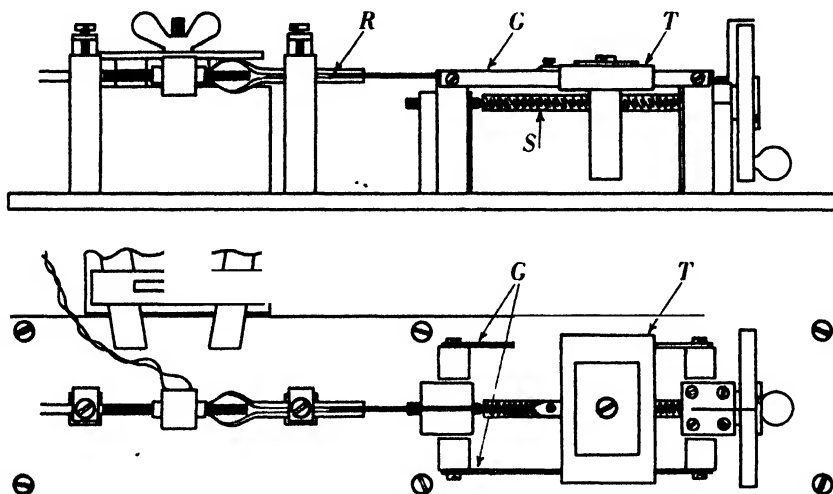


Figure 2. The interferometer.

oscillator, shaded in the figure, was put in the thin-walled tube having a bore of 1.2 mm., and the reflector was moved along inside the thick-walled capillary. In this manner a single oscillator was made to serve for several capillaries of various diameters. To maintain a stable vibration the rod must be fixed at its centre. The readiest method of mounting was to glue a narrow tissue-paper girdle round the middle of the rod. By sliding the needle into the tube a fairly rigid clamping of this girdle was secured, and at the same time the efficiency of production of the sound-waves was not impaired by excessive clamping.

The reflectors were made of soft metal (brass and copper), and satisfactory reflecting surfaces were obtained by filing on a fine grindstone. A scheme was devised whereby the reflector would not be rotated as it moved forward under the action of the turning handle; the reaction would be withstood by a rigid pillar. A diagram of the interferometer apparatus is shown in figure 2. The screw *S* is made to drive a table *T* along a pair of guides *GG*, the reflector *R* being attached to the table.

§ 3. METHODS OF MEASUREMENT

Although various ways of measuring the changes in the circuit currents with movement of the reflector were actually tried, the only reliable results were obtained when readings were taken with a galvanometer in the grid circuit. Connected across the galvanometer was a variable shunt for choosing the range of deflections desired, and a backing battery circuit to balance out the steady direct current.

In absorption measurements it is necessary to keep the power of the source constant when the supersonic intensity is measured with the reflector at various distances away. Klein and Hershberger⁽⁷⁾ suggest that this condition is satisfied if the exciting e.m.f. is maintained constant irrespective of the reaction of the air column. To check this suggestion, the oscillating voltage across the exciting coil was measured with an anode e.m.f. bend valve rectifier, and it was then seen that the exciting e.m.f. remained fairly constant for all positions of the reflector. As the periodic changes in the e.m.f. produced by the gradual movement of the reflector were small, it was assumed that the relation between the changes of current and the variations of the exciting voltage would be linear. Thus the amplitude of the variations of the grid current was taken to represent the amplitude of the sound-waves at the particular location of the reflector. It is admitted that the precision to be attained in absorption measurements in which a moving reflector and reaction on the source is used is not as great as that attained in a method in which the reflector is fixed and the space between it and the source traversed with a hot wire or other measurer of the amplitude in the air waves; but the introduction of such an instrument into the interior of these narrow tubes would have been impossible. A Sullivan dynatron-absorption wave-meter was used to measure frequency. This gave readings accurate to 0.1 per cent.

As the velocity varies with temperature it is necessary to measure the latter accurately when the velocity of sound is to be measured. Neither a thermometer nor a thermojunction could be introduced into the air enclosure, so the only possible procedure was to place a thermometer or thermocouple near the interferometer, and to satisfy oneself that the temperature measured was actually equal to the temperature of the enclosure. The only methods of supplying heat to the air in the tube and thus altering the temperature would be (1) joule heating of the exciting coil, (2) eddy-current heating of the source, and (3) direct heating of the air by sound-waves. The fact that, within the limits of experimental error, the results of wave-length measurements did not vary as the reflector was moved seemed to indicate that heating of the air in the course of a set of measurements did not appreciably raise the temperature in the tube.

§ 4. RESULTS

The natural logarithms of the differences between successive extreme readings of the galvanometer as the reflector is moved are plotted against the number of half-wave-lengths. The slope of the resulting graph represents the absorption

coefficient or attenuation per wave-length. Introducing the wave-length as determined from the locations of successive peaks gives us the amplitude-absorption coefficient per cm. The energy-absorption coefficient is twice as great. Each of the four graphs, figure 3, relates to a single tube at four frequencies. Actually the

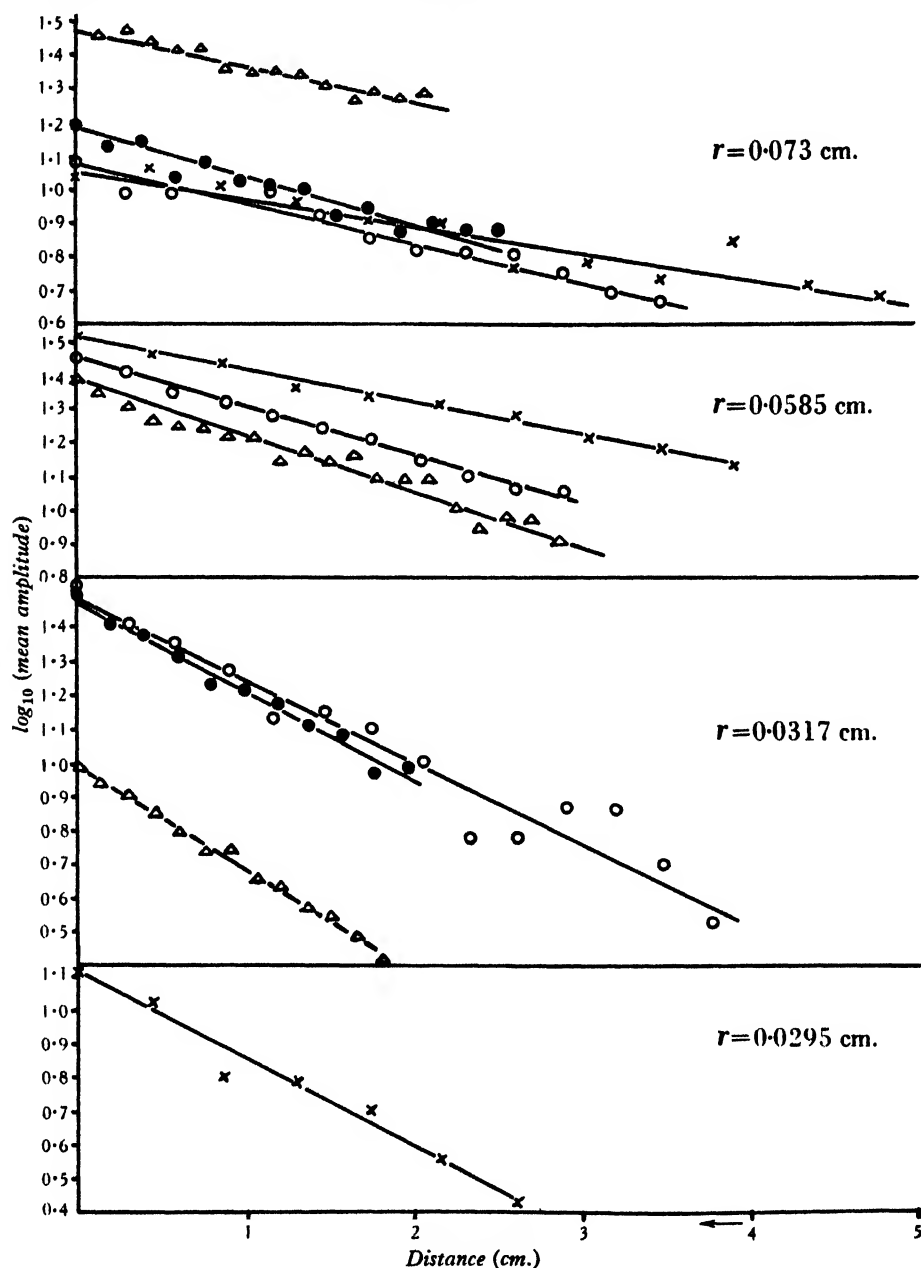


Figure 3. Variation of amplitude with distance. \times , 39.1 kc./sec.; \circ , 58.0 kc./sec.; \bullet , 90.0 kc./sec.; \triangle , 115.0 kc./sec.

logarithms plotted on the graphs are to the base 10, so that the amplitude-absorption coefficient is 2.3 times the slope. The velocity and absorption coefficients are grouped in the table, together with the corresponding values deduced from the Rayleigh theory, which are included for comparison.

Frequency (kc./sec.)	Tube radius (cm.)	Wave- length (cm.)	Tem- perature (° C.)	Reduced velocity (m./sec.)		Amplitude-absorp- tion coefficient	
				Practical value	Theoretical value	Practical value	Theoretical value
39.1	0.073	0.871	16.7	330.4	329.3	0.18	0.053
	0.0585	0.868	14.7	329.2	328.7	0.22	0.061
	0.0295	0.843	17.2	319.8	325.8	0.52	0.121
58.0	0.073	0.582	14.5	329.4	329.7	0.27	0.071
	0.0585	0.576	14.7	325.5	329.3	0.33	0.082
	0.0317	0.576	14.4	325.5	327.7	0.55	0.151
90.0	0.073	0.384	19.8	333.1	330.0	0.32	0.090
	0.0317	0.380	19.6	333.0	328.1	0.60	0.191
115.0	0.073	0.297	18.3	329.6	330.4	0.25	0.100
	0.0585	0.294	18.1	326.1	330.0	0.38	0.115
	0.0317	0.293	18.0	325.1	328.4	0.73	0.212

§ 5. DISCUSSION OF RESULTS

Rayleigh's version of Kirchhoff's theory recognizes two distinct cases, (1) that in which a quantity h is small compared with the wave-length, and (2) that in which h is comparable with the radius r of the tube. The quantity h has the value $2\pi \sqrt{(2\nu/\omega)}$, where ν is the kinematic viscosity and ω the pulsatace; this simplifies to $1.4/\sqrt{f}$, where f is the frequency, for air at 17° C. The quantity h will therefore have its highest value for the minimum frequency we are using. For these conditions

$$h_{\max.} = 1.4/\sqrt{40,000} = 0.007 \text{ cm.}$$

It is thus obvious that the conditions in question belong to the first case considered by Rayleigh.

The velocity c' appropriate to this case is given by

$$c' = \left(1 - \frac{h}{4\pi r}\right) c,$$

where c is the open-air velocity, and the absorption coefficient α is given by

$$\alpha = \frac{h}{4\pi r} \frac{\omega}{c} = \frac{1}{rc} \sqrt{\frac{\omega\nu'}{2}},$$

where ν' is a value of the kinematic viscosity slightly enhanced to allow for thermal conduction. The theoretical values are given in the table for comparison with the experimental values.

§ 6. CONCLUSIONS

Velocity. The measurements indicate that at the frequencies used and with tubes having a bore of 1 mm. the velocity deviates very little from the normal velocity.

Absorption. The practical values for the absorption coefficient were much in excess of the theoretical values. It was noticed that the ratio of the two quantities was very constant throughout the series. The mean of this ratio was just over 3, which is about the same as that found at low frequencies.

To sum up: (1) the absorption of supersonics in narrow tubes, within the range of radii and frequencies considered, satisfies the theory as regards the effect of frequency and radius, but its magnitude is much in excess of that determined theoretically; and (2) the velocity of supersonics in narrow tubes within the range decreases with the radius in a similar manner to that predicted by theory.

The value for the kinematic viscosity obtained from tables is for a slow direct flow and may be quite different from the value which applies to high-frequency air vibrations. The viscosity may in fact be a function of the frequency, although within the range that we have covered little variation is apparent. If this conclusion is not correct, there must be some other form of damping which has not been considered by the theorists.

§ 7. ACKNOWLEDGEMENT

The author wishes to offer his best thanks to Dr E. G. Richardson for suggesting this piece of research and for helpful criticism during the course of it.

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DISCUSSION

Mr H. L. PENMAN. In a number of the curves the points are not randomly distributed about the mean line, and in the third set, particularly for $v = 58$ kc./sec., there is a definite periodicity, the amplitude increasing as the length of air column increases. What is the source of this modulating frequency of about 20 kc./sec., which seems to have a negative absorption coefficient? Can it be due to reflection at the open end of the capillary tube?

The main point of interest arising out of the paper is the need for a reconsideration of the causes of absorption of sound in gases. The inadequacy of existing

interpretations has been shown in tube measurements at audio-frequencies and supersonic frequencies, and for free propagation at supersonic frequencies. If there is such a thing as an oscillatory viscosity which is greater than the kinematic viscosity, it is somewhat disconcerting to find that its value appears to be independent of frequency, there being no appreciable change between 200 c./sec. and 115,000 c./sec. Would it be possible to measure this viscosity by measuring the flow through a vibrating nickel tube?

If this high-value oscillatory viscosity cannot be established, it would seem that an overhaul of the Rayleigh-Kirchhoff theory is needed, and it might be profitable to replace the conception of the medium as a structureless jelly obeying Boyle's law by taking into account the fact that the medium is a molecular aggregate whose parts are in rapid motion, that the gas is imperfect, and that, in addition to viscosity, thermal conductivity and diffusion will tend to annul the effects of an impressed adiabatic pressure wave. As the molecules are not without structure it may be necessary to consider also the changes in internal energy due to collisions, and the interactions of the components where the gas is not homogeneous. In this connexion it is interesting to recall the large increases in the absorption coefficient of air when small amounts (0.5 per cent) of water vapour are present.

AUTHOR'S REPLY. I do not attach any importance to the regular variations in the graphs which Mr Penman points out, since the circuit current fluctuated somewhat in consequence of the vibrations of the laboratory. This would account for the points being deflected a little from the mean straight line. I quite agree that practical results seem to indicate that the coefficient of viscosity is independent of the frequency, but I do not see how the high-frequency value could be measured by the flow of gas through a vibrating nickel tube.

ATTENUATION AND GROUP RETARDATION IN THE IONOSPHERE

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ABSTRACT. Expressions are derived from the Appleton-Hartree formula for the specific attenuation and group velocity at any given height, in a layer with a vertical electronic gradient, for a wave of any given frequency at vertical incidence in the presence of an oblique magnetic field. They are then used to study the overall attenuation and group retardation of a wave which either is reflected from the layer, or penetrates through it to be returned from a denser layer above. To do this in detail, a definite type of layer has to be assumed, and particular values have to be chosen for the frequency of the wave and the direction and magnitude of the earth's magnetic field, so that the results can be compared with typical experimental data obtained by the usual $P'f$ and $P't$ technique. The analysis shows that, as one would expect from general physical principles, the attenuation and group delay for a wave near to the critical escape frequency occur mainly in the region of maximum density in the layer, and also justifies the use of absorption and equivalent-height measurements to deduce an estimate of the collisional frequency of the electrons in this region. The problem is worked out in detail for one frequency for the extraordinary wave, for values of the earth's field and the angle of the dip corresponding roughly to the values for London, and for a parabolic and a sine-squared law of electronic density. The work falls into four main sections: (a) the derivation of the integrals from the Appleton-Hartree formula; (b) the effect of the type of the layer on the form of the integrals; (c) the application of a graphical method of integration, involving the initial transformation of the integrals to a form in which they can be accurately evaluated; (d) the detailed working out of a numerical example, with a discussion of the general conclusions to be drawn from it. It is hoped that the fundamental results for the specific attenuation and group velocity, on which the rest of the paper is based, may prove useful in other investigations.

§ 1. INTRODUCTION

IT is well known from ionospheric observations made at vertical incidence by the usual $P'f$ technique, that the absorption of a wireless wave increases very rapidly when the frequency approaches the critical frequency corresponding to the maximum density in the layer. In general the increase in absorption occurs simultaneously with the rapid increase in the observed equivalent height of the layer at the end of the $P'f$ run. In a similar way when a $P't$ run is taken, the equivalent height of a layer may show a rapid increase in value, with an accompanying weakening of the echoes, due to the presence of an intermediate layer in which the density increases so that the critical frequency approaches the wave frequency. In this case, although the wave may still penetrate and be reflected at the upper layer, it will suffer heavy

absorption, and the group retardation will cause an apparent increase in the equivalent height of the upper layer.

Eckersley⁽¹⁾ has suggested that when such conditions occur, the measurements of increased absorption and equivalent height may be used to estimate the collisional frequency of the electrons in the region of the intervening layer. Such a method assumes, however, that the attenuation and group retardation are largely independent of the type of layer involved, the major part occurring in the region of maximum density. Although this seems probable on general physical grounds, it was felt that it would be useful to confirm the conclusion by working out the overall attenuation and group retardation in a particular case, by using the Appleton-Hartree formula as a basis for the analysis. In the course of the analysis, explicit forms of the specific attenuation and group velocity are obtained which may be of interest in other connexions, and they are therefore given here in sufficient detail to enable them to be available for such use.

The Appleton-Hartree formula has already been discussed, notably by Ratcliffe⁽²⁾ and Mary Taylor⁽³⁾, and the general properties of the function for the refractive index have been studied for various values of the constants involved, including the absorption coefficient. In this paper it is assumed that the absorption coefficient is so small, that all powers higher than the first can be everywhere neglected. With this fundamental assumption, when the Lorentz term is taken to be zero, in conformity with the view now generally accepted, exact expressions for the specific attenuation and group velocity at any given electronic density in the layer can be derived by a long but straightforward process. In order to integrate the effect over the length of the path in the layer, the relation between the density and the height in the layer has to be known, and the integrals so obtained have to be transformed before they can be applied to the accurate computation of attenuation and increase of equivalent height, for frequencies near to the critical escape frequency.

§ 2. GENERAL OUTLINE OF THE ANALYSIS

For convenience a list of the symbols to be used will first be given; it will serve to summarize the relations existing between them.

f is the wave frequency,

λ the wave-length in free space,

c the velocity in free space,

N the electronic density,

z the height, measured above the lower edge of the layer, at which the density N occurs,

e the electronic charge, and

m the electronic mass.

$f_0 = Ne^2c^2/\pi m$, the critical frequency corresponding to the density N ;

z_0 is the height at which the maximum density in the layer occurs,

H the earth's magnetic field, and

θ the angle H makes with the vertical.

$f_H = eH/2\pi mc$, the gyromagnetic frequency;

$\tau = f_H/f$, and is a function of f ;

$\zeta = f_0^2/f^2$, and is a function of f and N (i.e. of z).

f_0 is the collisional frequency of the electrons at the height z ,

β is a constant of the order of $\frac{1}{2}$, according to Burnett⁽⁴⁾;

$\alpha = f_c/\beta\pi f$, and is the absorption coefficient;

$\zeta' = \zeta(1 - i\alpha)$, i.e. the complex form taken by ζ when α is not zero but very small,*

and

$\tau' = \tau(1 - i\alpha)$, the corresponding complex form of τ .

U is the group velocity at the height z ,

μ the complex refractive index at the height z ,

μ_R the real part of μ ,

μ_I the imaginary part of μ , so that $\mu = \mu_R + i\mu_I$,

P' the equivalent path in the layer,

$h' = P'/2$, the equivalent height of the layer, and

T is the total group time in the layer, so that $P' = cT$.

In terms of this notation the Appleton-Hartree formula may be written

$$\mu^2 = \frac{(1 - \zeta')(1 - \tau'^2 - \zeta') - \frac{1}{2}\zeta'\tau'^2 \sin^2\theta \pm \zeta'\sqrt{\frac{1}{4}\tau'^4 \sin^4\theta + \tau'^2 \cos^2\theta (1 - \zeta')^2}}{(1 - \tau'^2) - \zeta'(1 - \tau'^2 \cos^2\theta)}$$

In this form it is derived directly from a quadratic equation for μ^2 , and it can be shown to be identical with the more familiar form of the Appleton-Hartree equation. Since we are neglecting all the terms involving α^2 etc., it follows at once that μ_R is obtained by merely replacing ζ' and τ' by ζ and τ respectively, while μ_I can be obtained as some function of ζ , multiplied by α , by expanding to the first power of α .

The specific attenuation at the height z is given by $\exp(-\mu_I \cdot 2\pi/\lambda)$, and thus the overall attenuation may be written $\exp(-A)$, where

$$A = \int \frac{2\pi}{\lambda} \mu_I dz$$

taken between appropriate limits. The group velocity U is given by

$$U = \frac{c}{\mu_R + f \frac{d\mu_R}{df}}$$

so that the element of the group time T corresponding to dz is given by

$$\begin{aligned} dT &= \frac{1}{c} \left[\mu_R + f \frac{d\mu_R}{df} \right] dz \\ &= \frac{\mu_R}{c} \left[1 + \frac{f}{2\mu_R^2} \frac{d(\mu_R^2)}{df} \right] dz. \end{aligned}$$

In evaluating $f \cdot d(\mu_R^2)/df$ we notice that in μ_R^2 the various functions of ζ and τ involved are all proportional to $1/f^n$, so that any such function F will give

$$f \frac{dF}{df} = -nF,$$

for example

$$f \frac{d(\zeta\tau^2)}{df} = -4\zeta\tau^2.$$

* Strictly speaking, $\zeta' = \zeta/(1 + i\alpha)$ and $\tau' = \tau/(1 + i\alpha)$.

Thus the final result for $f.d(\mu_R^2)/df$ will not involve f explicitly. The overall equivalent path P' is given by $\int cdT$, so that

$$\nu' = \int \mu_R \left[1 + \frac{f}{2\mu_R^2} \frac{d(\mu_R^2)}{df} \right] dz$$

between the same limits.

The process of evaluating the integrands of our two integrals, though straightforward, involves a long reduction to express them as functions of ζ , and only the final results will be given here. These can be conveniently summarized in the form of a table for quick reference, and for comparison of the cases for the ordinary and extraordinary waves. First, however, we must give a set of polynomials in ζ which are derived in the reduction process, and which form the basis of all the computations. They may be written

$$\begin{aligned} I_1 &= [(2 - \tau^2 + \tau^4) + 3\tau^2 \cos^2 \theta - \tau^4 \cos^2 \theta] \\ &\quad - 2\zeta [2 - \tau^2 + 3\tau^2 \cos^2 \theta] + 2\zeta^2 [1 + \tau^2 \cos^2 \theta], \\ I_2 &= [3\tau^4 \sin^4 \theta - \tau^6 \sin^4 \theta + 8\tau^2 \cos^2 \theta] \\ &\quad - 2\zeta [\tau^4 \sin^4 \theta + 12\tau^2 \cos^2 \theta - 2\tau^4 \cos^2 \theta \sin^2 \theta] \\ &\quad + 4\zeta^2 \tau^2 \cos^2 \theta [6 - \tau^2 \sin^2 \theta] - 8\zeta^3 \tau^2 \cos^2 \theta, \\ I_3 &= 2(1 - \tau^2)^2 - \zeta [4(1 + \tau^4 \cos^2 \theta) - 5\tau^2(1 + \cos^2 \theta)] \\ &\quad + \zeta^2 [2(1 - 4\tau^2 \cos^2 \theta) + \tau^4 \cos^2 \theta(1 + \cos^2 \theta)] + 2\zeta^3 \tau^2 \cos^2 \theta, \\ I_4 &= [\tau^4 \sin^4 \theta + 2\tau^2 \cos^2 \theta(1 + \tau^2)] - \zeta \tau^2 \cos^2 \theta [\tau^4 \sin^4 \theta + 6(1 + \tau^2 \cos^2 \theta)] \\ &\quad + \zeta^2 \cdot 2\tau^2 \cos^2 \theta [3 - \tau^2 + 4\tau^2 \cos^2 \theta] - \zeta^3 \cdot 2\tau^2 \cos^2 \theta [1 + \tau^2 \cos^2 \theta]. \end{aligned}$$

Table I introduces a number of new symbols which are functions of ζ , and serves both to define them and to explain their use. In the expressions for the extraordinary wave, the upper sign in terms such as $1 \mp \tau$ always refers to the condition $\tau < 1$, and the lower sign to $\tau > 1$.

The reflection point, where the group velocity is zero, is given by $\zeta = 1$ for the ordinary wave; and by $\zeta = 1 \mp \tau$ for the extraordinary wave; thus in both cases reflection occurs when $\delta = 0$. As $\delta \rightarrow 0$, Y , H and K remain finite, but X becomes proportional to δ . P and Q are defined to include the $\delta^{\frac{1}{2}}$ factor so as to make them finite at the limit when $\delta = 0$, and the integrands in A and P' have their infinities, for which $\delta = 0$, isolated in the factor $\delta^{\frac{1}{2}}$ in the denominator. The P and Q functions being finite over the whole range of ζ are very suitable for the further study of the integrals, and it is useful to know the end values, which are as follows:

Initially, when $\zeta = 0$, $P = 0$ and $Q = 1$ for both waves.

At the reflection point, $\delta = 0$. For the ordinary wave, $P = Q = \text{cosec } \theta$.

For the extraordinary wave,

$$P = \frac{Q}{1 \mp \tau/2} = \frac{1}{(1 \mp \tau)} \left[\frac{8}{1 + \cos^2 \theta} \right]^{\frac{1}{2}}.$$

Table 1

Ordinary wave	Extraordinary wave
$Y = (1 - \tau^2) - \zeta (1 - \tau^2 \cos^2 \theta),$ $Z = \sqrt{(\frac{1}{2}\tau^4 \sin^4 \theta + \tau^2 \cos^2 \theta (1 - \zeta)^2)},$	
$X = (1 - \zeta) (1 - \tau^2 - \zeta) - \frac{1}{2}\zeta\tau^2 \sin^2 \theta + \zeta Z,$	$X = (1 - \zeta) (1 - \tau^2 - \zeta) - \frac{1}{2}\zeta\tau^2 \sin^2 \theta - \zeta Z,$
$H = \zeta I_1 - \frac{\zeta I_2}{2Z},$	$H = \zeta I_1 + \frac{\zeta I_2}{2Z},$
$K = I_3 - \frac{\zeta I_4}{2Z},$	$K = I_3 + \frac{\zeta I_4}{2Z},$
$\delta = 1 - \zeta,$	$\delta = 1 - \frac{\zeta}{1 \mp \tau},$
	$P = \frac{\delta^{\frac{1}{2}} H}{2 [X Y^3]^{\frac{1}{2}}},$
	$Q = \frac{\delta^{\frac{1}{2}} K}{2 [X Y^3]^{\frac{1}{2}}}.$
For specific attenuation	$\mu_I = \frac{\alpha P}{2 \delta^{\frac{1}{2}}}.$
For group velocity	$\frac{U}{c} = \frac{\delta^{\frac{1}{2}}}{Q}.$
For overall attenuation	$A = \int \frac{\pi \alpha P}{\lambda \delta^{\frac{1}{2}}} dz.$
For equivalent path	$P' = \int \frac{Q}{\delta^{\frac{1}{2}}} dz.$

As $\delta \rightarrow 0$, $P/Q \rightarrow 1$ for the ordinary wave, and $P/Q \rightarrow (1 \pm \frac{1}{2}\tau)^{-1}$ for the extraordinary wave. Thus if the last part of the integrand near to the end value is predominant, measurements on the overall attenuation and group retardation will give a simple way of measuring α , and hence f_c the collisional frequency, in the region of maximum density.

In the computation of P and Q for the ordinary wave, a difficulty occurs at the value $\zeta_c = (1 - \tau^2)/(1 - \tau^2 \cos^2 \theta)$, where $Y = 0$, since when $\tau < 1$, this value occurs between $\zeta = 0$ and 1 , but it will be found that X , H , and K also are zero in such a way that the P and Q functions are continuous through the point. For the extraordinary wave $\zeta_c > 1 - \tau$ though it < 1 , and it therefore lies outside the range $\zeta = 0$ to $1 - \tau$; while when $\tau > \sec^2 \theta$ and ζ_c is between $\sec^2 \theta$ and $1 + \tau$, i.e. within the range $\zeta = 0$ to $1 + \tau$, the P and Q functions are continuous through ζ_c for the extraordinary wave. By the usual methods the values of P and Q at ζ_c can be determined, but in practice it is only necessary to compute values a little way on either side of ζ_c , since we know that the functions are continuous through the point.

The integrands of our two integrals, though explicitly given in terms of ζ , are actually functions of z by virtue of the relation between ζ and z , and to consider the integrals further we must now investigate the nature of this relation.

3. THE CHOICE OF THE GRADIENT OF ELECTRONIC DENSITY

It would be possible to take any empirical relation which could be represented graphically, without assuming that it has any simple analytical form, and to plot our P and Q functions, which are expressed in terms of ζ , as functions of z by purely graphical means. This method of attack would, however, lead to a very unwieldy process for studying the effect of approaching near to the critical escape frequency for the layer assumed. Moreover, it would be almost impossible by such purely graphical means to obtain the accuracy required for deciding the point at issue.

It is therefore better to choose one or two typical kinds of layer which can be represented analytically as a function of ζ and z , and as P and Q are expressed explicitly in terms of ζ , it is more convenient to convert the integral so that the integration is performed with respect to ζ instead of z . This will also lead to simpler conditions for reflection and penetration, the wave being reflected or penetrating according as the maximum density in the layer is greater or less than that corresponding to $\zeta = 1$ or $1 \mp \tau$ for the ordinary and extraordinary waves respectively. Three types of layer will therefore be considered.

(a) A layer in which the initial density N is zero, the initial gradient dN/dz also is zero, and N increases indefinitely with z . Since for a given frequency ζ is proportional to N , a simple layer of this type is the square-law layer which can be represented by

$$\zeta = kz^2.$$

This gives

$$dz = -\frac{d\zeta}{2k^{\frac{1}{2}}\zeta^{\frac{1}{2}}}.$$

For this type of layer the waves are always reflected, since we assume no upper limit to N .

(b) A layer in which the initial density is zero, but the initial gradient is finite and gradually decreases until a maximum density in the layer is obtained. A simple example is the parabolic layer for, which we may write

$$1 - \frac{\zeta}{\zeta_0} = \left(1 - \frac{z}{z_0}\right)^2,$$

where ζ_0 is the maximum value of ζ , i.e. of $(f_0)^2/f^2$, and occurs at a height z_0 . z_0 is thus half the total thickness of the layer, which is symmetrical about the height $z = z_0$. This leads to

$$dz = \frac{z_0}{2\zeta_0^{\frac{1}{2}}(\zeta_0 - \zeta)^{\frac{1}{2}}} d\zeta.$$

For the ordinary wave there is reflection when $\zeta_0 > 1$, and the upper limit of the integrals is $\zeta = 1$. When $\zeta_0 < 1$ there is penetration, and the upper limit is $\zeta = \zeta_0$. For the extraordinary wave the condition is $\zeta >$ or $< 1 \mp \tau$.

(c) A layer similar to (b) in possessing a maximum density, but having also an initial zero gradient which increases, and then decreases again to zero at the point of maximum density. The simplest type is the sine-squared layer given by

$$\frac{\zeta}{\zeta_0} = \sin^2\left(\frac{\pi}{2} \frac{z}{z_0}\right).$$

Here ζ_0 and z_0 have meanings similar to those in (b), and the layer is again symmetrical about $z = z_0$. This leads to

$$dz = \frac{z_0}{\pi} \frac{1}{\zeta^{\frac{1}{2}} (\zeta_0 - \zeta)^{\frac{1}{2}}} d\zeta,$$

and the conditions for reflection or penetration are the same as before.

We see that in case (a) the differential dz becomes infinite when $\zeta = 0$, while in case (b) it does so when $\zeta = \zeta_0$. Case (c) combines both properties, dz being infinite when $\zeta = 0$ and $\zeta = \zeta_0$. As we should expect, when $\zeta = 0$, dz has the same form as for the square-law layer except for a constant, and when $\zeta = \zeta_0$, it has the same form as for the parabolic layer. When the layer is dense enough to reflect the waves, our integrands also become infinite at the upper limit, as we have seen, where $\delta = 0$, but although the integrands can thus have three poles, the integrals themselves are finite, except when the two poles at $\zeta = \zeta_0$ and $\delta = 0$ occur together, i.e. when the wave frequency is the critical escape frequency.

Thus considering, for instance, the ordinary wave, we have the scheme shown in table 2.

Table 2

$\zeta_0 > 1$	Reflection. Integral between the limits 0 and 1. $\zeta < \zeta_0$, $\delta = 0$ when $\zeta = 1$. Integral finite.
$\zeta_0 < 1$	Penetration. Integral between the limits 0 and ζ_0 . At the upper limit $\zeta = \zeta_0$ but $\delta \neq 0$. Integral finite.
$\zeta_0 = 1$	Critical frequency. At the upper limit $\zeta = \zeta_0$ and $\delta = 0$. Integral infinite.

As $\zeta \rightarrow \zeta_0$ when $\zeta_0 = 1$, the total attenuation and equivalent path both increase rapidly. The infinity in the integral should be rounded off, and its occurrence in the analysis is due to neglect of the higher powers of α , and to the fact that the conditions assumed in deriving the formula for the refractive index become invalid in this limiting case. But we can evaluate the integrals for values of ζ_0 closer and closer to the values 1 or $1 \mp \tau$, and compare the calculated rapid increase in total attenuation and equivalent path with the results obtained experimentally in the region of the critical frequency.

In order to study this critical region more carefully, it is convenient to replace ζ_0 by $1 + l$ and $(1 \mp \tau)(1 + l)$ for the ordinary and extraordinary waves respectively for the case of reflection, so that $l = 0$ at the critical frequency, and l can have any positive value; and to replace ζ_0 by $1 - l$ and $(1 \mp \tau)(1 - l)$ for penetration, where $l < 1$. Thus l may be regarded as a parameter defining the nearness of approach to the critical condition.

We are now in a position to rewrite our integrals to include the effect of the type of layer chosen, by writing the relation between dz and $d\zeta$ as

$$dz = \phi(\zeta) d\zeta,$$

where the form of the function $\phi(\zeta)$ is determined by the choice of layer as above. In the case of reflection we will consider the total path to include the reflected wave,

and similarly in the case of penetration we will include the path of the transmitted wave as it goes out through the upper half of the layer. By virtue of the symmetry in the layer about the height $z = z_0$ —we need not consider further here the square-law layer of case (a)—this merely involves multiplying the integrals by 2, so that they become

$$2 \int_0^{1 \text{ or } 1 \mp \tau} \frac{\pi \alpha}{\lambda} \frac{P}{\delta^{\frac{1}{2}}} \phi(\zeta) d\zeta \quad \text{and} \quad 2 \int_0^{1 \text{ or } 1 \mp \tau} \frac{Q}{\delta^{\frac{1}{2}}} \phi(\zeta) d\zeta$$

for reflection, and

$$2 \int_0^{(1-l) \text{ or } (1 \mp \tau)(1-l)} \frac{\pi \alpha}{\lambda} \frac{P}{\delta^{\frac{1}{2}}} \phi(\zeta) d\zeta \quad \text{and} \quad 2 \int_0^{(1-l) \text{ or } (1 \mp \tau)(1-l)} \frac{Q}{\delta^{\frac{1}{2}}} \phi(\zeta) d\zeta$$

for penetration.

In dealing with the attenuation integrals, we must remember that the absorption coefficient α is really a function of the height z , since the collisional frequency f_c in which we are interested is known to be so, and if we know the law of its variation with height, we can embody this in the integral. But if we assume that the variation is small over the range of height with which we are concerned, we may take α outside the integral; in any case we may interpret the final value of α so obtained as an average value. To avoid further complications we will make this approximation here, pointing out that as in the sequel it will appear that most of the attenuation does take place in the region of maximum density, the assumed value of α is appropriate to that region.

§ 4. THE TRANSFORMATION OF THE INTEGRALS

In general, the integrals have to be solved by graphical means, although in some cases it may be found possible to represent the P and Q functions, to a fair degree of accuracy, by simple expressions that will lead to integrals which can be solved analytically. When we adopt the graphical method, however, we find that it is a difficult matter to estimate the areas under our curves because of the presence of the infinite values discussed above. As we shall need to measure the areas with the greatest accuracy in the cases in which the greater part of the area lies in the region of the pole at $\delta = 0$, we must find some method of removing the poles from the integrands.

The necessary transformations involved are rather more difficult in the case of the sinc-squared layer owing to the extra pole at $\zeta = 0$, but actually in practice they can be quite quickly applied, and for the purpose of estimating the area under the curve, by counting squares or by using a planimeter, it is more satisfactory to work with a curve which is finite over the whole range. In giving these transformations we shall only state the initial integral, the substitutions used, and the resulting transformed integral. For purposes of comparison we shall give the results for both the parabolic layer and the sine-squared layer; in the latter case the process is a modification of the former case. The results are given for reflection and penetration,

but we need to write out in detail only the cases of attenuation. We have therefore four cases to consider.

Case A: parabolic layer; reflection.

$$A = 2 \frac{\pi\alpha}{\lambda} \int_0^{1 \text{ or } 1 \mp \tau} \frac{P}{\delta^{\frac{1}{2}}} \frac{z_0}{2\zeta_0^{\frac{1}{2}}} \frac{1}{(\zeta_0 - \zeta)^{\frac{1}{2}}} d\zeta.$$

Now put

$$\zeta = 1 - \gamma^2 \quad \text{or} \quad (1 \mp \tau)(1 - \gamma^2),$$

and then

$$\xi = \frac{\log_e [1 + \gamma/\sqrt{l}]}{\log_e [1 + 1/\sqrt{l}]},$$

and we get

$$A = 2 \frac{\pi\alpha}{\lambda} z_0 \frac{\log_e [1 + 1/\sqrt{l}]}{\sqrt{(1+l)}} \Big|_0^1 P \frac{\sqrt{l+\gamma}}{\sqrt{(l+\gamma^2)}} d\xi.$$

Case B: parabolic layer; penetration.

$$A = 2 \frac{\pi\alpha}{\lambda} \int_0^{(1-l) \text{ or } (1 \mp \tau)(1-l)} \frac{P}{\delta^{\frac{1}{2}}} \frac{z_0}{2\zeta_0^{\frac{1}{2}}} \frac{1}{(\zeta_0 - \zeta)^{\frac{1}{2}}} d\zeta.$$

Now put

$$\zeta = (1-l)(1 - \gamma^2) \quad \text{or} \quad (1 \mp \tau)(1-l)(1 - \gamma^2),$$

and then

$$\xi = \frac{\log_e [1 + \gamma\sqrt{\{(1-l)/l\}}]}{\log_e [1 + \sqrt{\{(1-l)/l\}}]},$$

and we get $A = 2 \frac{\pi\alpha}{\lambda} z_0 \frac{\log_e [1 + \sqrt{\{(1-l)/l\}}]}{\sqrt{(1-l)}} \int_0^1 P \frac{\sqrt{l+\gamma}\sqrt{(1-l)}}{\sqrt{\{l+(1-l)\gamma^2\}}} d\xi.$

Case C: sine-squared layer; reflection.

$$A = 2 \frac{\pi\alpha}{\lambda} \int_0^{1 \text{ or } 1 \mp \tau} \frac{P}{\delta^{\frac{1}{2}}} \frac{z_0}{\pi \zeta^{\frac{1}{2}}} \frac{1}{(\zeta_0 - \zeta)^{\frac{1}{2}}} d\zeta.$$

Now put

$$\zeta = 1 - \gamma^2 \quad \text{or} \quad (1 \mp \tau)(1 - \gamma^2),$$

then

$$\gamma = 1 - \chi^2$$

and

$$\chi = 1 - \phi,$$

and lastly

$$\xi = \frac{\log_e [1 + \phi/\sqrt{l}]}{\log_e [1 + 1/\sqrt{l}]},$$

and we get

$$A = 2 \frac{\pi\alpha}{\lambda} \cdot \frac{4z_0}{\pi} \log_e \left[1 + \frac{1}{\sqrt{l}} \right] \Big|_0^1 \frac{P}{\sqrt{(2-\chi^2)}} \frac{\sqrt{l+\phi}}{\sqrt{(l+\gamma^2)}} d\xi.$$

Case D: sine-squared layer; penetration.

$$A = 2 \frac{\pi\alpha}{\lambda} \int_0^{(1-l) \text{ or } (1 \mp \tau)(1-l)} \frac{P}{\delta^{\frac{1}{2}}} \frac{z_0}{\pi \zeta^{\frac{1}{2}}} \frac{1}{(\zeta_0 - \zeta)^{\frac{1}{2}}} d\zeta.$$

Now put $\zeta = (1-l)(1-\gamma^2)$ or $(1 \mp \tau)(1-l)(1-\gamma^2)$,

then $\gamma = 1 - \chi^2$

and $\chi = 1 - \phi$,

and lastly $\xi = \frac{\log_e [1 + \phi \sqrt{\{(1-l)/l\}}]}{\log_e [1 + \sqrt{\{(1-l)/l\}}]}$,

and we get

$$A = 2 \frac{\pi \alpha}{\lambda} \cdot \frac{4z_0}{\pi} \frac{\log_e [1 + \sqrt{\{(1-l)/l\}}]}{\sqrt{(1-l)}} \int_0^1 \frac{P}{\sqrt{(2-\chi^2)} \sqrt{\{l+(1-l)\gamma^2\}}} d\xi.$$

To get the corresponding values for the equivalent path P' , we have only to omit the factor $\pi\alpha/\lambda$ and to replace P by Q .

In every case the transformed integral is between the limits 0 and 1, and it can be shown that the integrand is finite over the whole range, even when $l=0$. The pole in the critical case in which $l=0$ has been shifted outside the integral in the logarithmic term. For the cases of reflection, the term $\log_e [1 + 1/\sqrt{l}]$ approaches zero as l becomes large, and the substitutions reduce to $\xi=\gamma$ and $\xi=\phi$ respectively. The values of the integrals approach zero, in correspondence with the fact that with a very dense layer the wave is reflected with very little penetration into the layer. For the cases of penetration, the term $\log_e [1 + \sqrt{\{(1-l)/l\}}]/\sqrt{(1-l)}$ approaches 1 as l approaches 1, i.e. for an infinitely sparse layer. The substitutions again reduce to $\xi=\gamma$ and $\xi=\phi$ respectively, and the total attenuation becomes zero, since the P function becomes zero over the whole range from $\xi=0$ to 1, while if ζ is equated to 0 in the value of Q the equivalent path reduces to $2z_0$ (going right through the layer without retardation).

Of course, well away from the critical frequency the substitutions in terms of ξ are hardly necessary in practice, and in the case of penetration as $l \rightarrow 0$ the substitutions for ξ reduce to those used in the case of reflection, but it seems better to express them formally as above, and then to use any convenient approximations in practice.

The general procedure for the case of the parabolic layer is to evaluate P or Q as a function of ζ and hence of γ . A set of values of ξ is then chosen, say 0, 0.1, 0.2 up to 1.0, and for each given value of l the corresponding values of γ are worked out. For these values of γ , the values of the functions of the type $P(\sqrt{l+\gamma})/\sqrt{(l+\gamma^2)}$ are tabulated, so that they can be plotted as ordinates with ξ as abscissae over the range 0 to 1. The area under the curve can then be measured with a planimeter.

For the sine-squared layer the process is slightly longer but equally straightforward. The values 0, 0.1 etc. of ξ having been chosen as before, ϕ is now the same as the corresponding γ in the parabolic case. We have then to tabulate χ and γ , and to work out the values of

$$\frac{P}{\sqrt{(2-\chi^2)}} \frac{\sqrt{l+\phi}}{\sqrt{(l+\gamma^2)}}$$

etc. from which to plot the final curves for the estimation of the areas as before. The detailed significance of these transformations, as regards the relation of the final variable ξ to the original variable z , will be considered when we discuss the practical

example which is to follow. We can however see from the form of our integrals the general conditions which must hold, if the assumption made by Eckersley in deriving the value for the collisional frequency is to be justified.

§ 5. DISCUSSION OF THE INTEGRALS

We have seen that for the extraordinary wave the end value of the Q function in the equivalent path integral is $(1 \mp \tau/2)$ times the end value of the P function in the attenuation integral. It is found convenient, therefore, in this case, in considering the integrals with respect to ξ , to include a factor $(1 \mp \tau/2)$ under the integral sign for the attenuation integral, so that we can more conveniently compare the areas when determining the values of the integrals graphically. We then call the areas under the curves in the two cases R and S respectively, for example in case A of a parabolic layer and reflection we write

$$\int_0^1 \left(1 \mp \frac{\tau}{2}\right) P \frac{\sqrt{l+\gamma}}{\sqrt{(l+\gamma^2)}} d\xi = R$$

$$\text{and} \quad \int_0^1 Q \frac{\sqrt{l+\gamma}}{\sqrt{(l+\gamma^2)}} d\xi = S.$$

Then as $l \rightarrow 0$, the two areas R and S , which remain finite, should approach one another in value. In the particular case we have chosen we now have

$$A = 2 \frac{\pi\alpha}{\lambda} z_0 \frac{\log_e [1 + 1/\sqrt{l}]}{\sqrt{(1+l)}} \frac{R}{(1 \mp \tau/2)}$$

$$\text{and} \quad P' = 2z_0 \frac{\log_e [1 + 1/\sqrt{l}]}{\sqrt{(1+l)}} S.$$

We must now relate A and P' to the experimentally observed change in the strength of the echo, due to the attenuation, and the equivalent height h' respectively. If the strength of the echo is represented in decibels by D with respect to zero attenuation as datum, we have from the expression of the overall attenuation as $\exp(-A)$ that

$$D = 20 \log_{10} [\exp(-A)] = -20 [\log_{10} e] A.$$

$$\text{Thus} \quad D = -20 (\log_{10} e) \frac{2\pi\alpha}{\lambda} z_0 \frac{\log_e [1 + 1/\sqrt{l}]}{\sqrt{(1+l)}} \frac{R}{(1 \mp \tau/2)}.$$

The equivalent height h' is simply $P'/2$, so that

$$h' = z_0 \frac{\log_e [1 + 1/\sqrt{l}]}{\sqrt{(1+l)}} S.$$

$$\text{Suppose now that we write} \quad \frac{D}{20 (\log_{10} e) 2\pi\alpha z_0 / \lambda} = y$$

$$\text{and} \quad \frac{h'}{z_0} = x,$$

$$\text{so that} \quad y = - \frac{\log_e [1 + 1/\sqrt{l}]}{\sqrt{(1+l)}} \frac{R}{(1 \mp \tau/2)}$$

$$\text{and} \quad x = \frac{\log_e [1 + 1/\sqrt{l}]}{\sqrt{(1+l)}} S.$$

As $l \rightarrow 0$ and R and S get very nearly equal,

so that
$$\frac{D}{h' 40 (\log_{10} e) \pi \alpha} \approx \frac{1}{1 \mp \tau/2}.$$

If we put
$$\lambda = \frac{c}{f} \quad \text{and} \quad \alpha = \frac{f_e}{\beta \pi f},$$

this gives
$$f_c = -\frac{D \beta c (1 \mp \tau/2)}{h' 40 \log_{10} e}.$$

This is the relation which Eckersley used, where D/h' is simply the slope of the $\{D, h'\}$ curve, which he found experimentally to be a straight line. It is obvious that the same relation follows if we take any of the other cases A to D of § 4, except, of course, that for the ordinary wave the factor $(1 \mp \tau/2)$ is replaced by 1.

The validity of the method therefore depends upon the assumption that the $\{y, x\}$ curve is a straight line whose slope is $-1/(1 \mp \tau/2)$. Now we can show that the $\{y, x\}$ curve does eventually become asymptotic to a line whose slope is $-1/(1 \mp \tau/2)$. In the example given above, the relation between y and x can be put in the form

$$y = -\frac{x}{1 \mp \tau/2} + C,$$

in which

$$C = \frac{\log_e [1 + 1/\sqrt{l}]}{(1 \mp \tau/2) \sqrt{(1+l)}} [S - R],$$

and from case A in § 4, it will be found that R and S can be expressed in terms of integrals with respect to γ , giving

$$\log_e \left[1 + \frac{1}{\sqrt{l}} \right] [S - R] = \int_0^1 \frac{Q - (1 \mp \tau/2) P}{\sqrt{(1+\gamma^2)}} d\gamma.$$

Now if we assume that $Q - (1 \mp \tau/2) P$ can be represented as a polynomial of the form $a_1 \gamma + a_2 \gamma^2 + a_3 \gamma^3 + \dots$ (since it is zero when $\gamma = 0$), the integral becomes tractable by the substitution $\gamma = \sqrt{l} \tan \theta$. It is then found that as $l \rightarrow 0$

$$C \rightarrow \frac{\sum (a_n/n)}{1 \mp \tau/2},$$

which is independent of l .

For the sine-squared layer the corresponding integral is

$$\int_0^1 \frac{Q - (1 \mp \tau/2) P}{\sqrt{(1-\gamma^2)} \sqrt{(1+\gamma^2)}} d\gamma,$$

and this with the substitution $\gamma^2 = \frac{1-l}{2} + \left(\frac{1+l}{2} \right) \sin \theta$

gives
$$C_{l \rightarrow 0} = \frac{1}{(1 \mp \tau/2)} \left[a_1 + \frac{2}{\pi} a_2 + \frac{1}{2} a_3 + \dots \right],$$

which also is independent of l .

The validity of the analysis will be borne out by the practical example in § 6, the point of which is to show that actually the $\{y, x\}$ curve does approach closely to the asymptote, well within the range of values which we can observe experimentally. The asymptote itself does not go through the origin, for it is found that the intercept C is quite appreciable on the scale on which the $\{y, x\}$ curves are drawn, but this will not affect results that are based on measurements of points which are effectively on the straight line. We proceed therefore to a typical practical example to illustrate the use of the analysis, and to justify the general conclusions we have drawn from it.

§ 6. A PRACTICAL EXAMPLE

The evaluation of the P and Q functions depends upon the computation, in any particular case, of the polynomials in ζ which we have called I_1 to I_4 , and as some of the terms in these expressions are positive and others are negative, the values of I_1 to I_4 can in special cases be much less than any of the individual terms. In these cases this implies that we must determine the coefficients in I_1 to I_4 to a considerable degree of accuracy. It therefore helps to choose values of τ and θ which will make this a relatively simple task, and as those coefficients involve τ and θ as functions of τ^2 , $\cos^2\theta$ and $\sin^2\theta$, we will choose $\tau^2 = 0.1$ and $\tan\theta = \frac{1}{3}$. This value of θ corresponds to an angle of dip of $71^\circ 34'$, which is of the order of the value of the dip at London. The value $\tau = 0.3162$ corresponds, for the value of the earth's magnetic field at London, to a wave-length of 70 m., which is in the region in which experimental observations have been made. With these values of τ and θ we have the following end values at the reflection point:

For the ordinary wave $\zeta = 1, \quad P = Q = 3.162.$

For the extraordinary wave $\zeta = 0.684, \quad P = 1.500, \quad Q = 1.263.$

P and Q are plotted as functions of ζ for the ordinary and extraordinary waves in figure 1. It will be seen that the functions for the ordinary wave are more difficult to handle than those for the extraordinary wave, owing to the rapid rise of the P and Q curves near to the reflection point. The significance of this rise will be considered in the general discussion in the next section, and here we will content ourselves with the detailed working out of the case of the extraordinary wave; this was the case cited by Eckersley. We need only to consider the case of reflection.

In cases A and C in § 4, the first substitution is $\zeta = (1 - \tau)(1 - \gamma^2)$, so we take a set of values of γ , namely 0, 0.1, up to 1, and work out the corresponding values of ζ . We can then read off values from the curves in figure 1, and draw out new curves of P and Q plotted against γ . These are given in figure 2. Now taking case A for the parabolic layer first, we choose a series of values of l , say 0.1, 0.01, 0.001, and taking each in turn, we work out, for a series of values 0, 0.1 up to 1 of ξ , the corresponding values of γ . For these values of γ we compute $(\sqrt{l+\gamma})/\sqrt{(l+\gamma^2)}$, and multiply each value by the corresponding values of P and Q read off figure 2, and finally we get a series of graphs of $(1 - \tau/2) P (\sqrt{l+\gamma})/\sqrt{(l+\gamma^2)}$ and $Q (\sqrt{l+\gamma})/\sqrt{(l+\gamma^2)}$ against ξ for each value of l . A set of such curves is shown in figure 3, and the areas under these curves are measured with a planimeter, and give the values of R and S .

For the sine-squared layer the calculations are similar, but slightly more involved owing to the extra χ and ϕ substitutions. In this case it is useful to draw graphs of $P/\sqrt{(2-\chi^2)}$ and $Q/\sqrt{(2-\chi^2)}$ as functions of ϕ , and these are given in figure 4. The set of curves for $\left(1-\frac{\tau}{2}\right)\frac{P}{\sqrt{(2-\chi^2)}}\frac{\sqrt{l+\phi}}{\sqrt{(l+\gamma^2)}}$ and $\frac{Q}{\sqrt{(2-\chi^2)}}\frac{\sqrt{l+\phi}}{\sqrt{(l+\gamma^2)}}$ for the determination of R and S is given in figure 5.

We can see from figures 3 and 5 that as l gets smaller, the area R approaches the value of S , although even for the smallest values shown, the difference in the areas is quite a large percentage of either area alone. But when we plot y against x , as in

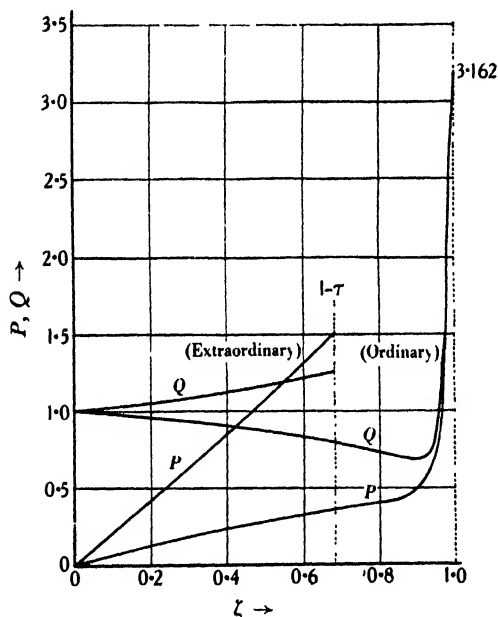


Figure 1. P and Q as functions of ζ for ordinary and extraordinary waves. $\tau = 0.3162$, $\tan \theta = \frac{1}{2}$.

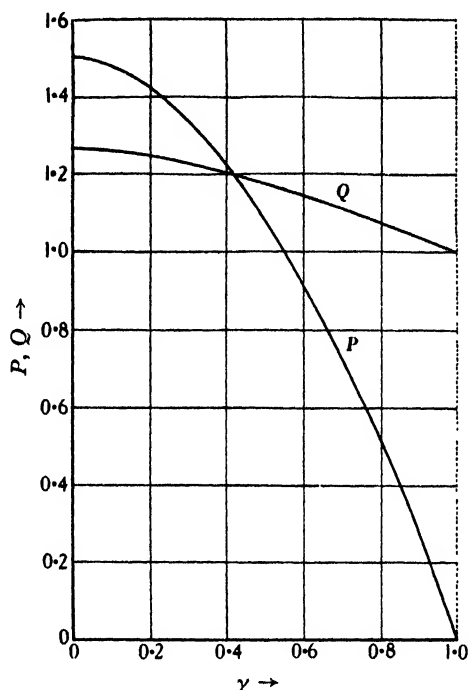


Figure 2. P and Q as functions of γ for extraordinary wave. $\tau = 0.3162$, $\tan \theta = \frac{1}{2}$.

figures 6 and 7, we see that the points lie on a straight line to a close approximation, even the point for $l = 0.1$ being only a small distance away from the line. Since, even at the smallest values of l , R is markedly different from S , the straight line does not go through the origin, but shows an appreciable value of the intercept C .

It is found from figure 2 that in our case P and Q can be represented closely by parabolic curves, so that $Q - (1 - \tau/2)P$ can be expressed as $a_1\gamma + a_2\gamma^2$. By determining from the curves the values of a_1 and a_2 , we can estimate the value of C by the analysis given in § 5, i.e.

$$C = \frac{a_1 + a_2/2}{1 - \tau/2} \quad \text{and} \quad \frac{a_1 + (2/\pi)a_2}{1 - \tau/2}$$

respectively, and actually the straight lines drawn in figures 6 and 7 are lines of slope

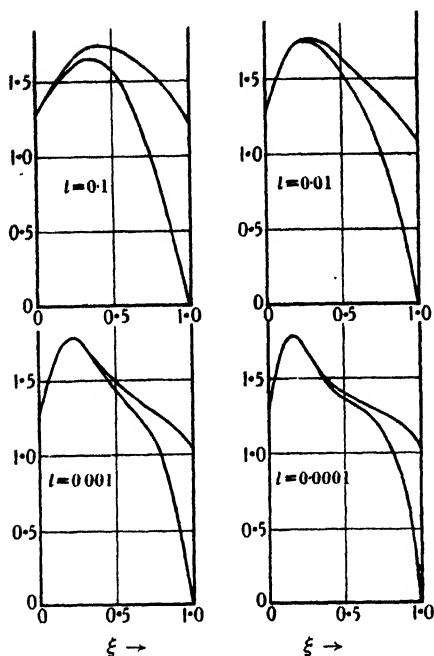


Figure 3. Curves for estimating R and S for parabolic layer for various values of l . Upper curves, $Q(\sqrt{l+\gamma})/\sqrt{l+\gamma^2}$; lower curves, $(1-\tau/2)P(\sqrt{l+\gamma})/\sqrt{l+\gamma^2}$.

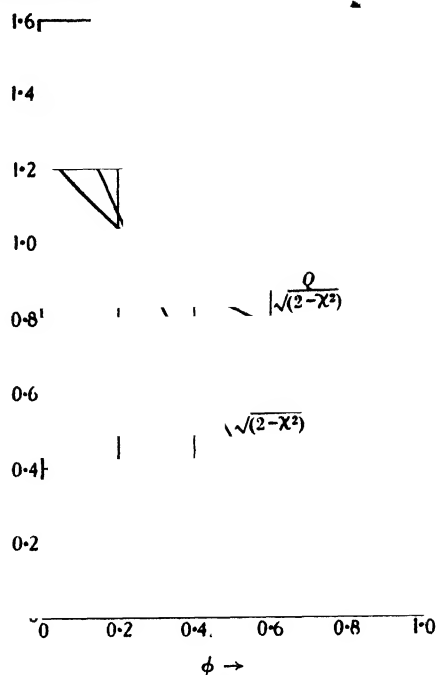


Figure 4. $P/\sqrt{2-x^2}$ and $Q/\sqrt{2-x^2}$ as functions of ϕ for extraordinary wave. $\tau=0.3162$, $\tan \theta = \frac{1}{2}$.

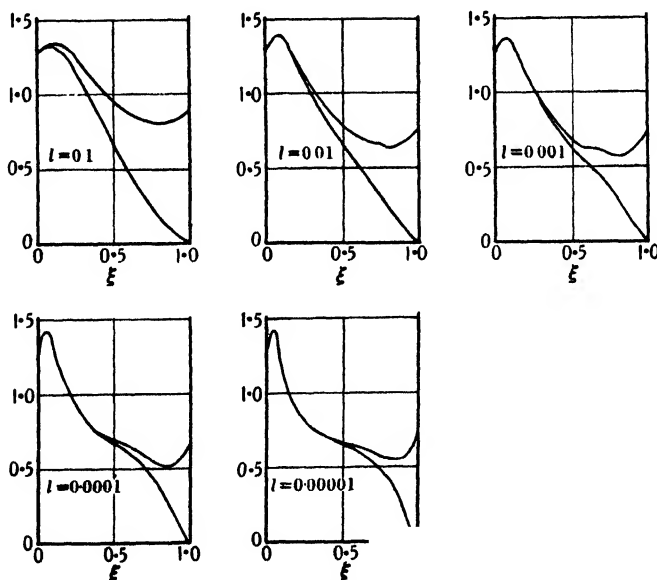


Figure 5. Curves for estimating R and S for sine-squared layer for various values of l .

Upper curves, $\frac{Q}{\sqrt{2-x^2}} \frac{\sqrt{l+\phi}}{\sqrt{l+\gamma^2}}$; Lower curves, $\frac{(1-\tau/2)P}{\sqrt{2-x^2}} \frac{\sqrt{l+\phi}}{\sqrt{l+\gamma^2}}$.

$-1/(1-\tau/2)$ with these computed intercepts. We thus have a good check on the accuracy of the graphical method and the general soundness of the analysis.

In both cases we can say that the $\{y, x\}$ curve approaches the asymptote for values of x greater than 2, i.e. for values of h' greater than $2z_0$. Assuming that the half-thickness z_0 of the layer is, say, 50 km., the curve therefore becomes effectively linear for increases of equivalent height greater than 100 km. In typical experiments increases of 400 or 500 km. are quite usual, and the experimentally obtained straight lines of D against h' are therefore explicable by the above analysis. It appears that the neglect of the higher powers of α in the analysis does not become of importance until l is made very small, and the frequency of the wave is exceedingly near to the

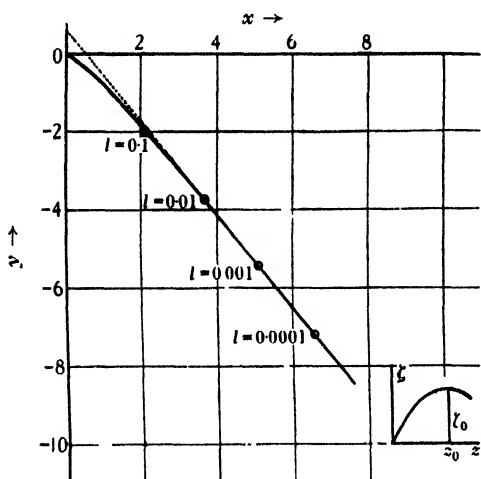


Figure 6. Curve showing the relation between y and x for parabolic layer.

$$y = \frac{D}{20 (\log_{10} e) 2\pi \alpha z_0 / \lambda}, \quad x = h/z_0,$$

$$(1 - \zeta/\zeta_0) = (1 - x/z_0)^2.$$

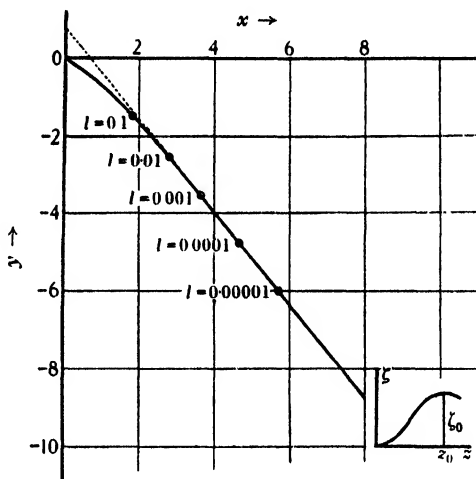


Figure 7. Curve showing the relation between y and z for sine-squared layer.

$$y = \frac{D}{20 (\log_{10} e) 2\pi \alpha z_0 / \lambda}, \quad x = h/z_0,$$

$$\zeta/\zeta_0 = \sin^2 (\frac{1}{2} \pi x/z_0).$$

critical frequency in the layer. The observed increases of equivalent height imply the small values of l we have assumed in deriving the curves. The closer spacing of the points along the line in figure 7, as compared with figure 6, shows the greater total attenuation and group time in the parabolic layer compared with the sine-squared layer for any given value of l , which is due to the fact that at any given height the density in the parabolic layer is greater than in the sine-squared layer.

It will be noticed that the analysis corresponds to the case of a $P't$ run, in which the wave-frequency is kept constant, and the density of the layer alters gradually in the course of time, in a manner given by the variation of l . But it is obvious that by using the $P'f$ technique, and considering the region near to the critical frequency of the layer, now considered constant, where the changes of f are small compared with f itself, the analysis can be interpreted to give the changes in attenuation and equivalent height near to the critical frequency in a $P'f$ run.

The fact that most of the attenuation and retardation near to the critical frequency takes place in the region of the maximum density, can be seen from figures 6 and 7 by considering, say, the points for $l=0.01$ and $l=0.001$. The extra attenuation in the case of $l=0.001$ must occur mainly in the small extra distance travelled in the layer very near to the level of the maximum density. Thus the straight line can be interpreted as giving a value of the collisional frequency in the region of the maximum density.

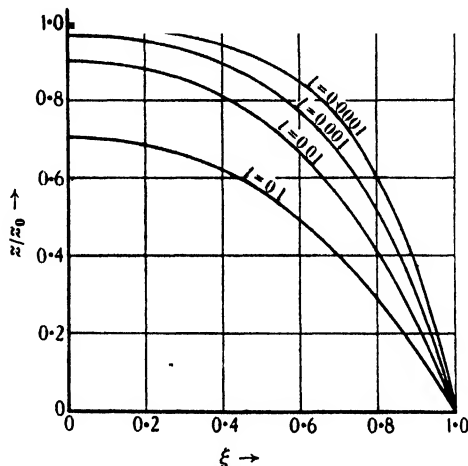


Figure 8. Curve showing the relation between ξ and z/z_0 for parabolic layer.

This point can be further seen by considering the significance of the transformations used in § 4. By taking case *A*, we can draw a set of curves of the original variable z in terms of the final variable ξ , for the various values of l we have chosen, and this is given in figure 8. By using these curves we can then see what part of the areas *R* and *S* originate from any given range of values of z , and it is obvious that most of the range of ξ corresponds to values of z in the region of the maximum density. In the case of the sine-squared layer this will be even more so, as the $\{z, \xi\}$ curve in the region $z=0$, $\xi=1$ will climb more steeply, on account of the initial zero gradient in the layer, involving the extra χ and ϕ substitutions in the transformations. We thus conclude from the analysis that the method suggested by Eckersley for determining the collisional frequency f_c is justified, and it remains only to consider some of the more general aspects of the analysis.

§ 7. GENERAL RESULTS OF THE ANALYSIS

The analysis gives explicit forms both for the specific attenuation and the group velocity at any height z , corresponding to any given ζ value in the layer. It is useful therefore to draw graphs of these, as functions of ζ , for the particular example we have considered above. For the specific attenuation we can take $P/\delta^{\frac{1}{2}}$, for the comparison of the ordinary and extraordinary waves, and for the group velocity we can take $\delta^{\frac{1}{2}}/Q$, which is equal to U/c .

From the curves for P and Q in figure 1 we therefore derive the curves given in figure 9. These curves show that up to any given height the ordinary wave travels faster than the extraordinary wave, the fact that the ordinary echo normally appears beyond the extraordinary echo in $P'f$ and $P't$ observations arising from the greater height to which the ordinary wave must go to be reflected. This also explains why in the presence of an intermediate layer not dense enough to reflect either wave, the order of the echoes reflected from an upper layer may be reversed, as a result of the greater delay suffered by the extraordinary wave in traversing the intermediate layer.

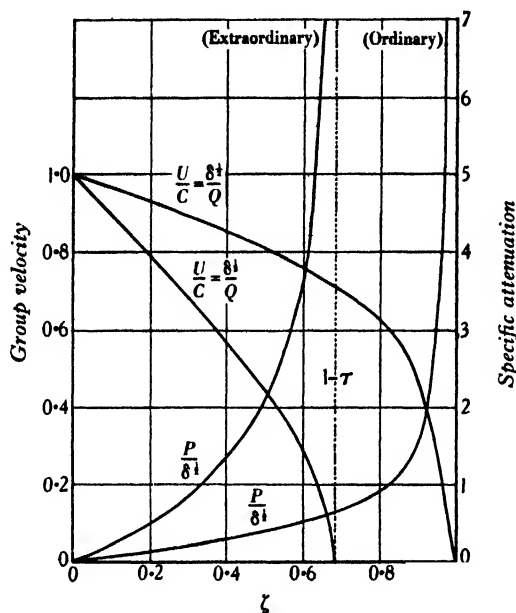


Figure 9. Group velocity and specific attenuation as functions of ζ . $\tau = 0.3162$, $\tan \theta = \frac{1}{3}$.

The specific attenuation at a given height is considerably greater for the extraordinary wave than for the ordinary wave, so that in general on such wave-lengths the ordinary echo is the stronger of the two. It is difficult however to determine the relation of the overall attenuation and group retardation for the two waves in any given case, without a closer examination of the kind given in the practical example above. The shapes of the P and Q curves vary considerably for different values of τ and θ , and in particular for small values of θ , for the ordinary wave, they show the rapid rise to a large end value as seen in figure 1. This end value is $\text{cosec } \theta$, and tends to ∞ as θ tends to zero and the field approaches the vertical, and the computation of the curve in this region needs special care. This rapid rise is associated with the value of ζ_0 when $\gamma = 0$.

In our practical example $\zeta_0 = 0.989$, and is very close to $\zeta = 1$. The curve in the region of $\zeta = 1$ is best computed by converting the polynomials I_1 to I_4 into functions of δ , equal to $(1 - \zeta)$, and as it may be of considerable interest to compute curves for

other values of τ and θ , these expansions are given here. Thus for the ordinary wave for which $\delta = 1 - \zeta$,

$$\begin{aligned} I_1 &= [\tau^2 \sin^2 \theta (1 + \tau^2)] - \delta [2\tau^2 \sin^2 \theta] + \delta^2 [2 (1 + \tau^2 \cos^2 \theta)], \\ I_2 &= [\tau^4 \sin^4 \theta (1 - \tau^2)] + \delta [2\tau^4 \sin^2 \theta (1 + \cos^2 \theta)] \\ &\quad - \delta^2 [4\tau^4 \cos^2 \theta \sin^2 \theta] + \delta^3 [8\tau^2 \cos^2 \theta], \\ I_3 &= [\tau^2 \sin^2 \theta (1 + \tau^2 + \tau^2 \sin^2 \theta)] - \delta [\tau^2 \sin^2 \theta (5 - 2\tau^2 \cos^2 \theta)] \\ &\quad + \delta^2 [2 (1 - \tau^2 \cos^2 \theta) + \tau^4 \cos^2 \theta (1 + \cos^2 \theta)] - \delta^3 [2\tau^2 \cos^2 \theta], \\ I_4 &= [\tau^4 \sin^4 \theta (1 - \tau^2 \cos^2 \theta)] + \delta [\tau^4 \cos^2 \theta \sin^2 \theta (4 + \tau^2 \sin^2 \theta)] \\ &\quad - \delta^2 [2\tau^4 \cos^2 \theta \sin^2 \theta] + \delta^3 [2\tau^2 \cos^2 \theta (1 + \tau^2 \cos^2 \theta)]. \end{aligned}$$

By means of these relations it was found possible to compute P and Q to an accuracy of 1 in 1000 for a value 0.990 of ζ , i.e. within 0.001 of ζ_0 .

If τ is made smaller, so that it approaches zero, the end value of P and Q remains at $\operatorname{cosec} \theta$, but in the limit the curve for Q approaches the horizontal line $Q = 1$, and the final rise is delayed until it becomes the line $\zeta = 1$. Our equations then reduce to the simple case of zero magnetic field;

$$\frac{U}{c} = \frac{\delta^{\frac{1}{2}}}{Q}$$

becomes
$$\frac{U}{c} = \delta^{\frac{1}{2}},$$

and since we then have
$$\mu_R^2 = 1 - \zeta = \delta,$$

$$U = c\mu_R$$

as it should.

If θ is made to approach zero while τ remains constant, the end value of P and Q for the ordinary wave approaches infinity, and it appears that in this case also the rise is delayed towards $\zeta = 1$; but in this case we approach the discontinuity at $\theta = 0$, i.e. vertical field, when the reflection at $\zeta = 1$ no longer occurs, and we go over to the longitudinal case with reflections at $\zeta = 1 - \tau$ and $1 + \tau$.

In a similar way we can check up for other special values of τ and θ . The general expressions we have developed also embrace values of ζ beyond the reflection point, and hold for the isolated real branches of the wave function which are known to occur. Thus the group-velocity analysis is strictly equivalent to that given by Goubau⁽⁵⁾ and by Rai⁽⁶⁾, and curves of the type given by Bajpai and Mathur⁽⁷⁾ can be derived from it.*

The method we have adopted of obtaining the fundamental ζ polynomials whose coefficients are functions only of τ and θ , and of defining the P and Q functions in terms of them, should be found helpful and instructive in following out the changes which occur as τ and θ are altered. Although this aspect of the problem has not yet been attacked in detail, it is obvious that such a set of curves would be very useful for studying generally the nature of propagation in the presence of a magnetic field.

* Actually Goubau, by using approximations, includes the Lorentz term in his analysis.

§ 8. ACKNOWLEDGEMENTS

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EMISSION BANDS OF SiCl_2 AND SnCl_2

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ABSTRACT. The discharge through flowing vapour of SiCl_4 , SnCl_4 , and SnCl_2 shows a number of regions of selective continuous emission, and, intimately connected with them, several sets of new bands. These appear under conditions unfavourable for the production of the known bands of SiCl and SnCl respectively. They are broad and diffuse, and have not the appearance of bands due to a diatomic emitter of low molecular weight. They are quite different from the known SiCl and SnCl bands as far as the anharmonic factor of the ground level of the molecule is concerned. They are therefore attributed to the triatomic molecules SiCl_2 and SnCl_2 respectively.

An analysis carried out on this assumption reveals two excited electronic levels of SiCl_2 ($\nu\nu = 28295$ and 29952), and one of SnCl_2 ($\nu = 22237$). The presence of the deforming (breathing) vibration ω_1 , and of the symmetrical valence vibration ω_2 are indicated both in the ground state and in the various excited states. The antisymmetric valence vibration is absent, in agreement with Herzberg-Teller's selection rules. For certain reasons ω_2' is smaller than ω_2'' , despite ω' being larger than ω'' in the corresponding excited terms of SiCl and SnCl . The energies of excitation and the values of ω_2'' of SiCl_2 and SnCl_2 show a close similarity to the corresponding constants of SiCl and SnCl respectively, and also the bond energies appear to be rather unaffected by the transition from the diatomic to the triatomic molecule. The later ones appear to be triangular.

§ 1. INTRODUCTION

IN this paper are described the spectra of the flowing vapours of SiCl_4 , SnCl_4 , and SnCl_2 . The spectra of SnCl_4 and SnCl_2 have been studied only with uncondensed discharge and with a constant pressure of the flowing vapour, while the spectrum of SiCl_4 has been taken under varying conditions of pressure and with condensed and uncondensed discharge. Previous work of this nature has been done by Jevons⁽¹⁾ in the case of CCl_4 , SiCl_4 , TiCl_4 , and BCl_3 and more recently for SiBr_4 ⁽²⁾. This work, however, does not deal with variations in spectra brought about by different conditions of excitation and pressure. It is shown in the experiments described below that the nature of the spectra, in most of these substances, undergoes certain radical changes under varying conditions of the pressure of the flowing vapour.

§ 2. EXPERIMENTAL

For each substance a separate discharge tube of the H pattern fitted with a quartz window has been used. These had the usual side bulbs containing phosphorus pentoxide and crushed sodium hydroxide. The substance was contained in another

side bulb with a stop cock for the regulation of the flow of the vapour. All substances investigated, except SnCl_2 , are liquids at ordinary temperatures. We have used $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ which melts at about 38°C . It was found that in vacuum the solid itself gave sufficient vapour pressure and it was not found necessary to heat it. Only in the case of SiCl_4 , since the use of aluminium electrodes gave rise to the well known AlCl bands⁽³⁾, nickel electrodes have been used. The discharge tube was connected to the high-vacuum apparatus, operated by a mercury diffusion pump which was backed by a rotary oil pump. The flow of the vapour was adjusted to give the desired pressure by having two stop-cocks on either side of the discharge tube. Pressures were measured on a MacLeod gauge. The tubes were run on a 0.25-kw. transformer delivering 15,000 v. For the condensed discharge a set of three ordinary Leyden jars arranged in parallel were used with a spark gap of about 2 mm. in series with the tube. The spectrum of SnCl_2 has been studied only in the uncondensed discharge. In all the cases the medium Hilger quartz spectrograph has been used to investigate the ultra-violet region of the spectrum, while for the visible region the Hilger constant deviation glass spectrograph has been employed. In the case of SiCl_4 attempts were made to photograph the spectrum on a three-prism quartz spectrograph with a Littrow mounting. This necessitated long exposures, during which it was found difficult to maintain the constancy of pressure. The plates have been measured on an Abbé comparator, using copper arc lines as standards. The wave-lengths of the beginning, maximum, and end of continuous emission bands have been determined from microphotometer records, which were obtained on a Zeiss recording microphotometer.

§ 3. THE EMISSION SPECTRUM OF SiCl_4

The spectrum of the discharge through flowing SiCl_4 vapour has been studied under different conditions of pressure and in each case with condensed and uncondensed discharge. With a pressure of about 0.5 mm. of mercury, the uncondensed discharge shows four maxima of continuous emission at $\lambda\lambda 4022$, 3250, 2560, and 2450, and the set of bands of SiCl due to the transition $\text{B} \rightarrow \text{x}$ ⁽⁴⁾. Jevons⁽¹⁾ records two regions of continuous emission between $\lambda\lambda 6300$ to 5300 and 4850 to 3100. The first region of continuous emission starts at about $\lambda 5200$. We have, however, regarded this as a continuation towards longer waves of the maximum at $\lambda 4022$, on the basis that the region in which the gap appears is such that here the plates that we have used are not sensitive and most of the molecules studied exhibit the same gap. The second region of the continuum between $\lambda\lambda 4850$ and 3100 recorded by Jevons, really consists of two continuous regions with a maximum at $\lambda 4022$, to which Jevons's first region of continuous emission belongs, and $\lambda 3250$, which, however, merge into one continuous whole at pressures higher than about 0.5 mm. of mercury. With pressures of 0.2, 0.1, and 0.05 mm. of mercury and with condensed and uncondensed discharge the continuous maxima at $\lambda\lambda 2560$ and 2450 disappeared and the SiCl bands⁽⁴⁾ due to the transitions $\text{C} \rightarrow \text{x}$ and $\text{D} \rightarrow \text{x}$ were observed. The two maxima on the longer wave-length side, i.e. $\lambda\lambda 4022$ and 3250, became weaker

in intensity as the pressure was reduced and were accompanied each by a set of narrow bands. Figure 1 is a reproduction of the plate showing these bands. In the condensed discharge they were further enhanced in intensity at the expense of the continua. A pressure of 0.05 mm. of mercury was found to be the most favourable for the production of these bands. The bands in the body of the maximum

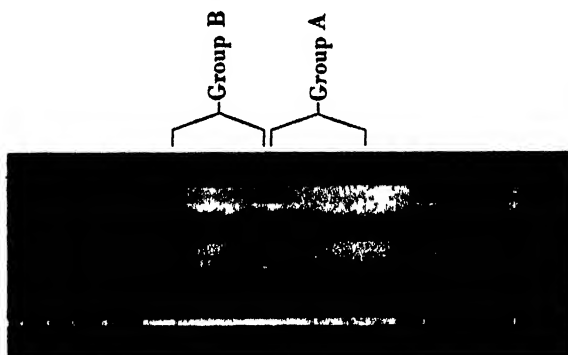


Figure 1. Spectrogram of SiCl_4 bands.

at $\lambda 4022$ are broad and diffuse, which fact makes it difficult to locate the heads. The bands in the maximum at $\lambda 3025$, on the other hand, are narrow and they also do not show any structure, but their heads in most cases could be more accurately located. In any case, on account of the low dispersion used, the possibility of the overlap of the heads due to different transitions is great. In both these sets the direction of degradation is difficult to ascertain with certainty. The measurements, however, have been made on the assumption that they are degraded towards longer waves. The data on the continuous regions are given in table 1.

Table 1

Long-wave-length limit			Maxima			Short-wave-length limit A.
A.	Kcal.	Electron-volts	A.	Kcal.	Electron-volts	
6500	44.0	1.9	4022	70.5	3.0	3550
3550	80.0	3.5	3260	86.7	3.8	3160
2620	108.0	4.7	2570	110.5	4.8	2535
2500	113.7	4.9	2450	116.0	5.0	2400

Table 2 contains the list of the bands observed in the first two continua. They represent the mean of three independent measurements. In the first set of bands the agreement between the three values is not so good, the discrepancy amounting in some cases to 2 Å. For the other set, however, it amounts to about 0.8 Å., so that the measurements are accurate to within 0.7 Å. in the first case and to 0.3 Å. in the second case. Exposures ranging from 15 min. to 1½ hr. were tried, but measurable plates were obtained with an exposure of 30 min. on the medium Hilger quartz spectrograph. An attempt was made to photograph the bands on a three-prism

Table 2

	λ_{air} (Å.)	Inten- sity	ν_{vac} (cm. ⁻¹)	Classification		$\nu_{\text{obs}} - \nu_{\text{calc}}$
				$(\omega_a \omega_b)'$	$(\omega_a \omega_b)''$	
Group A						
<i>e</i>	3916.7	—	25524	(0-0)'	(5-1)''	+ 6
<i>n</i>	3881.3	—	25757	(0-0)'	(5-0)''	- 9
<i>d</i>	3844.0	—	26007	(0-0)'	(4-1)''	- 1
<i>m</i>	3807.8	—	26254	(0-0)'	(4-0)''	- 2
<i>r</i>	3770.6	—	26513	(0-0)'	(3-1)''	+ 1
<i>l</i>	3734.3	—	26771	(0-0)'	(3-0)''	+ 11
<i>b</i>	3702.0	—	27005	(0-0)'	(2-1)''	- 1
<i>k</i>	3667.3	—	27260	(0-0)'	(2-0)''	+ 6
<i>a</i>	3633.8	—	27512	(0-0)'	(1-1)''	+ 6
<i>j</i>	3602.6	—	27750	(0-0)'	(1-0)''	- 4
<i>h</i>	3564.1	—	28050	(0-0)'	(0-1)''	- 6
<i>i</i>	3533.2	—	28295	(0-0)'	(0-0)''	- 9
Group B						
<i>L</i>	3482.1	(1)	28710	(2-1)'	(4-1)''	- 1
<i>x</i>	3476.1	(2)	28760	(2-0)'	(4-0)''	+ 1
<i>s'</i>	†3471.9?	(2)	28795			
	3464.4*	(2)	28857	(1-0)'	(3-0)''	- 7
<i>B</i>	3451.2	(2)	28967	(3-0)'	(4-1)''	- 9
<i>T</i>	3446.5	(2)	29009	(2-1)'	(4-0)''	+ 7
<i>C</i>	3440.2*	(3)	29069	(2-0)'	(3-1)''	- 6
<i>P</i>	3435.2*	(1)	29102	(1-1)'	(3-0)''	- 5
				(3-1)'	(4-1)''	- 4
				(1-0)'	(2-1)''	- 7
<i>H</i>	3428.6	(1)	29158	(3-0)'	(4-0)''	- 9
<i>K</i>	3422.3	(1)	29212	(0-0)'	(1-1)''	- 6
<i>w</i>	3417.7	(1)	29251	(2-1)'	(3-1)''	- 4
<i>y</i>	3410.3	(1½)	29315	(2-0)'	(3-0)''	- 12
<i>s</i>	3406.3*	?	29349	(1-1)'	(2-1)''	+ 5
<i>p</i>	3399.0	(3)	29412	(1-0)'	(2-0)''	- 8
				(0-1)'	(1-1)''	- 16
				(0-0)'	(1-0)''	0
<i>S</i>	3388.7	(2)	29501	(2-0)'	(2-1)''	- 8
<i>D</i>	3383.2	(2)	29549	(1-1)'	(2-0)''	- 9
<i>O</i>	3377.1*	(1½)	29603	(1-0)'	(1-1)''	- 6
<i>A</i>	3370.7	(1)	29659	(0-1)'	(1-0)''	- 10
				(4-1)'	(4-0)''	+ 6
				(0-0)'	(0-1)''	- 5
<i>g</i>	3366.2*	(3)	29699	(2-1)'	(2-1)''	- 11
<i>v</i>	3359.7	—	29756	(2-0)'	(2-0)''	- 1
<i>I</i>	3355.4	—	29794	(1-1)'	(1-1)''	- 16
<i>r</i>	3347.9*	(3)	29861	(1-0)'	(1-0)''	+ 4
<i>f</i>	3343.3	(3)	29902	(3-0)'	(2-1)''	- 6
				(0-1)'	(0-1)''	- 3
				(2-0)'	(1-1)''	- 2
<i>R</i>	3331.7	(4)	30006	(1-1)'	(1-0)''	- 2
<i>E</i>	3326.2*	(3)	30056	(3-1)'	(2-1)''	- 6
<i>z</i>	3320.5	(4)	30107	(3-0)'	(2-0)''	- 2
				(1-0)'	(0-1)''	- 7
				(0-1)'	(0-0)''	- 11
<i>N</i>	3316.7*	?	30142	(4-0)'	(2-1)''	+ 3
<i>X</i>	3309.6*	—	30205	(2-1)'	(1-1)''	- 5
				(2-0)'	(1-0)''	0
				(3-0)'	(1-1)''	- 5
<i>u</i>	3304.1	(4)	30257	(1-1)'	(0-1)''	+ 6
<i>V</i>	3293.3*	(4)	30356	(1-1)'	(0-1)''	+ 6

Table 2 (cont.)

	λ_{air} (Å.)	Inten- sity	ν_{vac} (cm^{-1})	Classification		$\nu_{\text{obs}} - \nu_{\text{calc}}$
				$(\omega_a \omega_b)'$	$(\omega_a \omega_b)''$	
Group B (cont.)						
<i>q</i>	3288.6*	(1)	30399	(1-0)'	(0-0)''	+ 2
				(4-1)'	(2-1)''	- 7
<i>c'</i>	3283.2*	(2)	30449	(4-0)'	(2-0)''	- 1
				(2-1)'	(1-0)''	- 9
					Cu?	
<i>Q</i>	†3279.7 3272.8*	? —	30482 30546	(2-1)'	(0-1)''	- 3
				(3-1)'	(1-1)''	- 16
<i>y</i>	3265.4*	(2)	30615	(3-0)'	(1-0)''	+ 6
				(1-1)'	(0-0)''	+ 17
<i>W</i>	3255.9	(4)	30705	(4-0)'	(1-1)''	+ 3
<i>G</i>	3250.7*	—	30754	(2-1)'	(0-1)''	+ 4
				(5-0)'	(2-0)''	- 4
<i>t</i>	3246.4	—	30795	(2-0)'	(0-0)''	- 2
<i>U</i>	3235.0*	(3)	30903	(3-0)'	(0-1)''	+ 2
				(4-1)'	(1-1)''	0
<i>b'</i>	3229.7*	(2)	30954	(4-0)'	(1-0)''	+ 4
				(5-1)'	(2-0)''	- 5
<i>Y</i>	3223.3*	(2)	31016	(5-0)'	(1-1)''	+ 6
				(2-1)'	(0-0)''	+ 18
<i>F</i>	3214.5	(2)	31100	(3-1)'	(0-1)''	- 2
<i>M</i>	3204.2	(8)	31200	(5-1)'	(1-1)''	- 11
<i>a'</i>	3174.9	(6)	31488	(4-0)'	(0-0)''	- 2
	†3158.1	(5)	31656			

† These bands have been measured only once and on one plate only and are, therefore, doubtful.

Capital and lower-case letters indicate the transitions in figures 3 and 4. Figures in brackets in second column indicate visually estimated intensities

quartz spectrograph giving higher dispersion, but this involved a much longer time of exposure during which it was not possible to maintain the optimum pressure of the flowing vapour. The spectra obtained on these plates were not sufficiently intense for measurements, but they enabled us to find that the bands did not show any resolution in their structure even at this higher dispersion of about 6 Å. per mm. in the region $\lambda\lambda 3275$ to 3200 . The twelve bands of group A can be arranged as shown in the table 3.

Table 3

$(\nu_a \nu_b)''$	(0-0)	(0-1)	(1-0)	(1-1)	(2-0)	(2-1)	(3-0)	(3-1)	(4-0)	(4-1)	(5-0)	(5-1)
$(\nu_a \nu_b)'$												
		(538)		(507)		(492)		(506)		(483)		
(0-0)	28050		27512		27005		26513		26007		25524	
	(245)		(238)		(255)		(258)		(247)		(233)	
	28295		27750		27260		26771		26254		25757	
		(545)		(490)		(489)		(517)		(497)		

The bands can thus be regarded as forming a single ν' progression and as having a mean doublet separation of 246 cm^{-1} . The $\Delta G''(\nu_a)$ values are irregular, but $\omega_{\frac{1}{2}}'' 540 \text{ cm}^{-1}$ indicates a rough correspondence with $\omega_{\frac{1}{2}}'' 530 \text{ cm}^{-1}$ of the ground

state of the diatomic molecule $\text{SiCl}^{(4)}$. The doublet separation of the ground state of SiCl is 208 cm^{-1} and this again suggests the possibility that the bands observed here might be due to a transition from an excited $^3\Pi$ inverted level with a separation of about 38 cm^{-1} to the ground $^3\Pi$ state of SiCl . This interpretation, however, has to be discounted for the following reasons:

(1) Although the $\Delta G''v_a$ values are not very regular and ω_3'' has a value which in view of the errors of observations may be assumed to agree quite well with the corresponding value in the ground state of SiCl , the second differences $\omega''x''$ which are of the order of 4.5 cm^{-1} in the latter case do not appear to present themselves in these bands.

(2) The analysis of the second set of the bands, as is shown later, also yields $\Delta G''(v_a)$ values similar to those of the first set of bands, and therefore suggests that both these two sets of bands have a common final state which is certainly different from the ground state of the SiCl molecule, but which has a close correspondence with it, so far as the frequency of vibration of the molecule is concerned.

(3) The bands are broad, those of group A particularly so, and they do not show any structure, at least with the instruments used, which is rather uncommon for a diatomic molecule of low molecular weight.

(4) These bands as well as those of group B are not excited under conditions which produce SiCl bands, but require particularly low pressures, and are more intense in the condensed discharge under which the SiCl bands get weaker in intensity. At relatively high pressures the bands disappear and merge into the continuous bands which they accompany.

In the bands of group B, doublets with a mean interval of 201.1 cm^{-1} as well as of 504 cm^{-1} can be picked out. The first doublet separation reminds us of the doublet separation in the ground state of SiCl , viz. 207.9 cm^{-1} , while the second is without doubt the same vibrational difference as we observe in the group A bands. As said above, the bands can be arranged in v' progressions which give first differences that can be identified with those of group A. It has not been possible, however, to arrange the bands in v' progressions having first differences comparable with the v' progressions of the $B \rightarrow X$ system⁽⁴⁾ of SiCl .

These peculiarities suggest that both groups of bands have a common emitter and arguments 3 and 4 given above indicate that this emitter in all probability is a multi-atomic one. Furthermore, the argument given under 2 suggests that the emitter is very probably the SiCl_2 molecule. It has been shown^(5,6) that the symmetric valence vibration in the ground state of many triatomic molecules has an order of magnitude comparable with the ground frequency of the corresponding diatomic molecule. For example, the ground frequencies of SO and SeO are 1118 and 910 cm^{-1} respectively, while those of the symmetric valence vibration of SO_2 and SeO_2 are 1128 and 901 cm^{-1} respectively^(5,6). From a comparison with data on Raman spectra similar relations have been shown to exist for H_2O and OH , CH_4 and CH , SnCl_4 and SnCl , BiCl_3 and BiCl , and many other pairs⁽⁵⁾.

Hence an attempt was made to analyse these bands, attributing them to a triatomic molecule. The analysis of the bands is displayed in table 4. The analysis

indicates that two modes of vibration are exhibited in the ground state^a of the molecule. We shall denote by ω_a'' and ω_b'' the frequencies connected with these two modes of vibrations and by $\Delta G''(v_a)$ and $\Delta G''(v_b)$ the vibrational term differences. In tables 5 and 6 we compare the vibrational term differences for the two sets of bands observed. The agreement between these term values for the two sets of bands

Table 5. $\Delta G''(v_a)$ values for ω_a mode of vibration

Band group	0-1	1-2	2-3	3-4	4-5
A	538	507	492	506	483
	545	490	491	517	497
	Mean 541.5	498.5	491.5	510.5	490.0
B	540	479	492	502	
	509	501	492	491	
	538	512	505		
	540	507			
	538	505			
	547	508			
	528	500			
		505			
	Mean 538.6	502.1	496.3	496.5	
Accepted Mean 540.0		500.3	493.9	503.5	490.0

Table 6. $\Delta G''(v_b)$ values for ω_b mode of vibration

Group A	Group B
245	253
238	257
255	258
258	247
247	249
233	251
	255
	242
	249
	249
	244
Mean 246.0	Mean 250.4
Accepted Mean 248.2	

is satisfactory and the slight discrepancies are within the experimental error. It has not been possible to arrange both sets of bands into one system. This, coupled with the fact that the two sets of bands differ in appearance, as has already been stated above, inclines us to regard them as two systems, both having the same final state, but having different excited states. The excited electronic level to which the bands of group B are due, again exhibits the same two modes of vibration as are found in the final state. If we denote, as before, by ω_a' and ω_b' the excited frequencies

with the two modes of vibrations and by $\Delta G'(\nu_a)$ and $\Delta G'(\nu_b)$ the excited vibrational term differences, we collect the data in tables 7 and 8.

Table 7. $\Delta G'(\nu_a)$ values for ω_a mode of vibration. Bands group B

0-1	1-2	2-3	3-4	4-5
443	394	346	339	311
444	407	357	342	305
449	399	350		
	404	358		
	396	351		
	403			
	396			
Mean 445.3	399.9	352.4	340.5	308

Table 8. $\Delta G'(\nu_b)$ values for ω_b mode of vibration. Bands group B

0-1	203, 191, 213, 195, 200, 203, 208, 211, 203, 207, 197, 184, 200
	Mean 201.1

The excited electronic level associated with the bands of group A does not exhibit any vibrational levels. It is difficult to say whether this is due to instability of the molecule in this state. This possibility is discussed later. The other possibility is the following. The vibration frequencies associated with this level are of an order of magnitude such that the differences between these and the frequencies of the

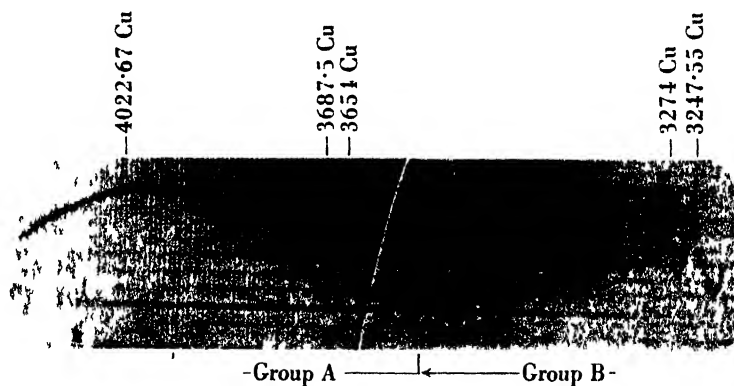


Figure 2 Microphotometer record of SiCl₄ bands

ground state result in bands which differ very slightly in wave-lengths. The breadth of the bands suggests this possibility. If, for example, ω_a' and ω_b' were about 500 and 200 cm⁻¹ respectively, and these values are possible on comparison with frequencies associated with the electronic level *A*, then a little calculation will show that the successive bands of a sequence will lie close together. The reproduced microphotometer curve given in figure 2 actually shows at least two or three maxima which are close together in each band.

Figure 3 Simple transitions of SiCl_4 bands.

The analysis proposed here, shows that the two band systems observed are, in all probability, due to SiCl_2 , and that they involve three electronic levels, namely, x , a ($28,034 \text{ cm}^{-1}$ above x), and A (29952 cm^{-1} above x). With level x are associated five vibrational levels belonging to one mode of vibration ω_a'' and one vibrational level belonging to ω_b'' . The level A is similarly associated with five vibrational levels belonging to the excited state of frequency ω_a' and one vibrational level belonging to the second mode of vibration ω_b' of the excited state. The spacings of the vibrational levels of the ω_a'' frequency are irregular, so that a correct evaluation of the anharmonic factor is not possible. Roughly $2\omega_a''x'' \simeq 12$ and $2\omega_a'x' \simeq 40$, indicating a large increase in the anharmonicity factor in the excited a state. Evidently no information is obtained for the anharmonicity factor for the frequency ω_b .

A non-linear triatomic molecule possesses three fundamental modes of vibration, viz. the total symmetric or deformation or breathing vibration ω_1 , the symmetric valence vibration ω_2 , and the antisymmetric valence vibration ω_3 . In table 9 we give some examples of the actual values of these vibrational frequencies for the

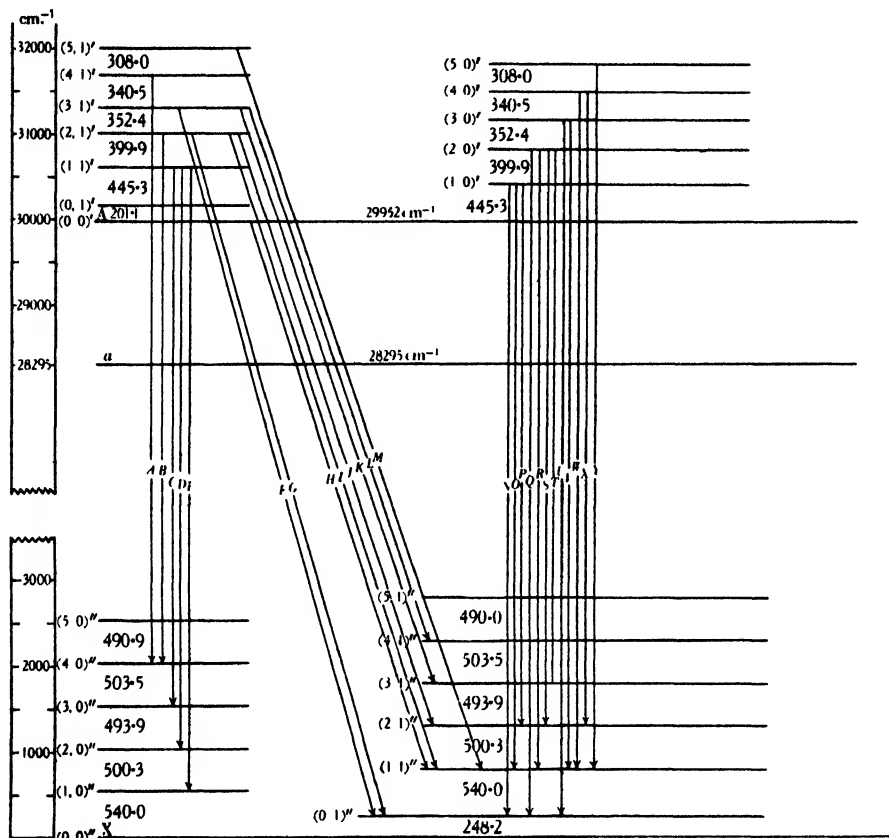


Figure 4. Cross and multiple transitions of SiCl_2 bands.

ground state of some such molecules. It appears as if ω_3 is always slightly larger than ω_2 , and ω_1 something less than half of ω_2 . This is true not only for the molecules in table 9 but also for others like H_2S , O_3 , Cl_2O , $\text{NOCl}^{(7)}$. It is interesting to see that this list comprises non-linear molecules of quite different structures, i.e. with an even as well as an odd number of electrons, with equal or unequal atoms linked to the central atom with a single or double bond. In all these cases nearly

Table 9

Molecule	ω_1	ω_2	ω_3
H_2O	1595.4	3600	3756
SO_2	524.0	1152	1361
NO_2	640.0	1370	1615
ClO_2	529.0	946	1109

the same ratio for ω_1 , ω_2 and ω_3 persists. As discussed elsewhere⁽⁶⁾, the reason for this uniformity may be that ω itself is more sensitive to the mass than to the forces or to the energy of the bond.

At the same time we know that in the transition from a diatomic radical like SO or SeO to a triatomic molecule like SO_2 or SeO_2 the symmetric valence vibration of the latter has almost the same value as the vibrational frequencies of the radical. For SO and SO_2 the values are respectively $\omega'' = 1150$, $\omega_2'' = 1128$, and $\omega' = 623$, $\omega_2' = 662$.

Considering the figures $\omega_a'' = 540$, $\omega_b'' = 248$, $\omega_a' = 445$, $\omega_b' = 201$, we find ω_b'' something less than half of ω_a'' . At the same time $\omega_a'' = 540$ is in close agreement with $\omega'' = 531$ of SiCl. Doubtless ω_a has to be identified with the symmetric valence vibration ω_3 , whereas ω_b is the breathing or deforming vibration ω_1 . This correlation receives support from the values of 425 of the total symmetric vibration of SiCl_4 , which corresponds to the symmetric valence vibration of a tetrahedron-like molecule⁽⁷⁾. The above values therefore indicate that SiCl_2 is a *non-linear* molecule.

A new feature is, however, added by the fact that ω_2' of SiCl_2 does not agree any longer with $\omega_a' = 660$ to 700 (according to the excited term considered) of SiCl. Molecules like SO and SO_2 both have an even number of electrons; in both the bond energies are weakened by excitation and hence $\omega_2' < \omega_2''$ and $\omega' < \omega''$. In SiCl_2 both p electrons of Si take part in the linkage, while in SiCl, however, one remains as an odd electron. For SiF it could be shown⁽⁸⁾ that this electron disturbs the linkage, in agreement with the theory developed earlier⁽⁹⁾. For SiCl the uncertainty of ω'/ω'' still prevents a correlation of the atomic and molecular terms, but doubtless the same conditions hold good for this molecule as for SiF. It is therefore by no means surprising, but in good agreement with theoretical conceptions, that in the odd numbered molecule SiCl we find $\omega' > \omega''$ but in the even numbered molecule SiCl_2 , as in SO_2 , $\omega_2' < \omega_2''$.

The similarity between ω'' of SiCl and ω_2'' of SiCl_2 is again in good agreement with the Heitler-London pair-bond theory of valency. In this conception the bonds are strongly localized in molecules possessing a pronounced central atom. This receives confirmation from considerations of bond energies. For SiCl the extrapolation of the vibrational levels give a rough value of about 4 e.v. for D (SiCl) which will be an upper limit. Parti and Samuel⁽¹⁰⁾ have shown that D (SiCl_2) may be roughly estimated as $3/5$ of D (SiCl_4). The energy of formation of gaseous SiCl_4 from the elements is given as 151 kcal./mol.⁽¹¹⁾, the sublimation energy⁽¹²⁾ of Si, is 47, $D(\text{Cl}_2) = 57.9$, and the heat of sublimation of SiCl_4 is 7.2 kcal./mol.⁽¹³⁾. By means of Born's cycle, 308 kcal./mol. is obtained for the energy of formation of SiCl_4 by combination of unexcited atoms. The value of the heat of sublimation of Si, however, appears to be rather inaccurate and too high. According to the above ratio, $D(\text{SiCl}_2)$ is 185 and the energy of a single $\text{Si}^{\text{II}}\text{—Cl}$ bond 92.5 kcal./mol. or 4 e.v. in good agreement with $D(\text{SiCl})$. The similarity of ω'' (SiCl) and ω_2'' (SiCl_2) may be considered as a consequence of this. The bond energy of SiCl_4 of course is not one-quarter of $D(\text{SiCl}_4)$. Exactly as in CCl_4 , the ground level of the molecule involves a Si atom in the excited configuration sp^3 . The value of the corresponding

5S term is not known for Si, but has been calculated⁽¹⁴⁾ as about 4 e.v. for C. The value of the D states belonging to the same configuration sp^3 , as well as the ionization potential of Si is about 33 per cent less than that of C⁽¹⁵⁾. Hence the excitation energy of the 5S term will be about 2.7 e.v. D (SiCl_4) being 13.4 e.v., $\frac{1}{4}$ ($13.4 + 2.7$) or about 4.0 e.v. obtains for the bond energy of the $\text{Si}^{\text{IV}}-\text{Cl}$ link. As always in such cases, involving the splitting of the s^3 group, the bond energy should increase slightly for the state of maximal valency, and hence our figures appear to be slightly incorrect, probably on account of too high a value of the heat of sublimation of silicon.

The determination of the dissociation energy of a polyatomic molecule by vibrational extrapolation is yet problematic. Still, as a first approximation it should be possible to obtain a rough estimate of the single bond energy from the extrapolation of the vibrational levels of the symmetric valence vibration alone, for which a number of levels are measured, neglecting at first the other modes. The thermochemical value of D_B ($\text{Si}-\text{Cl}$) being in agreement with D' (SiCl), such an extrapolation again should give a value of about 3 to 4 e.v. On account of the similarity of the two frequencies ω'' (SiCl) and ω_2'' (SiCl_2), $\omega_2''x_2''$ therefore should again have a value of the order of $\omega''x''$ of SiCl , i.e. about 2.2. The vibrational levels of the ground state obtained for ω_2 mode of vibration are rather irregular and perturbed. The accepted means of $\Delta G''(v_a)$ values have been listed in table 5 and the first value of $2\omega_2''x_2''$ of about 12 cm^{-1} which appears in the analysis as well of the A group as of the B group bands, may be due to real perturbations, and not only to overlapping of bands involving other vibrational levels of either electronic state. Also the remaining values are too few in number to permit an extrapolation with any degree of accuracy. From the experience of the band spectra of diatomic molecules it is known that even a far larger number of observations, more often than not, yields an absolute value of D which is incorrect by 25 to 50 per cent, just on account of the inaccuracy of ωx . It is, however, worthy of note that the remaining second differences of the B-group bands which appear to be the least perturbed, give a mean value of 5.1 or $\omega_2''x_2'' = 2.55$, rather near to the expected one. But it goes without saying, that no conclusion can be drawn from this fact at present.

One more conclusion can, however, be drawn. The value of 4 e.v. has been determined thermochemically for the bond energy. The excitation energy of the two levels a and A is 3.5 and 3.7 e.v. respectively. The dissociation energy of both the excited levels appears to be very small. For level a , this follows from the fact, that the excited vibrational levels do not appear, and for level A, from the large value of $\omega_2'x_2'$. Actually an extrapolation with the values $\omega_2' = 445$ and $\omega_2'x_2' = 34.2$ would yield a value of $D'(A) = 0.3$ e.v., which we may consider as the upper limit. It is therefore probable that both excited states involve unexcited dissociation products or at the most Cl in its $^2P_{\frac{1}{2}}$ term, about 0.1 e.v. above $^2P_{\frac{3}{2}}$, its ground state.

Contrary to the spectra of SO_2 and SeO_2 recently investigated, the antisymmetric valence vibration is not involved in the bands of SiCl_2 . This is in agreement with Herzberg and Teller's⁽¹⁶⁾ theory, according to which transitions involving an antisymmetric frequency should occur if at all, with low intensity, and only if $\Delta\nu_{\text{antisym}}$.

is even. This latter postulate indeed holds good in SeO_2 . Incidentally the fact that odd and even combinations of the two frequencies are involved in the bands of SiCl_2 also shows that none of them is ω_3 . Herzberg and Teller's selection rule⁽¹⁶⁾ is the more valid the smaller the change in the internuclear distance on excitation. The appearance of ω_1 in the spectrum of SiCl_2 and its absence in those of SO_2 and SeO_2 may well be due to the fact that this distance changes much less in the present case. This possibility receives confirmation from the fact that ω_2' is comparatively less smaller than ω_2'' . For SiCl_2 , ω_2' is about 25 per cent of ω_2'' , for SO_2 and SeO_2 about 45 per cent. In the present state of knowledge it would be premature to do more than just to point out this possibility. It may well be that the difference in the modes of vibration involved in the spectra is due to quite other reasons, e.g. to the fact that SO_2 and SeO_2 are investigated in absorption and SiCl_2 in emission.

A few new bands of SiCl have been observed on some heavily exposed plates, which fit into the existing scheme. These are given in table 10. Except on one heavily exposed plate which shows three or four very faint bands probably due to SiO (not checked by measurements) no SiO bands have been registered on any of the plates of SiCl_4 vapour.

Table 10

λ_{alt} (Å.)	Intensity	ν_{calc} (cm. ⁻¹)	Classification $\nu'-\nu''$	$\nu_{\text{obs}} - \nu_{\text{calc}}$ *
3240.3	(3)	30853	P_1 0-6	- 5.0
3219.0	(2)	31057	P_2 0-6	- 8.9
3188.4	(6)	31355	P_1 0-5	- 12.1
3134.5	(1)	31894	P_1 0-4	+ 13.5
3115.4	(1)	32089	P_2 0-4	+ 0.6
2896.6	(1)	34513	P_2 2-2?	- 10.0
2852.2	(1)	35050	P_2 2-1?	+ 0.4

* Calculated values are from the following equation⁽⁴⁾:

$$\nu = 34102.7 + \{(701.5x' - 1.40x'^2) - (535x'' - 2.20x''^2)\}, \quad \text{where } x' = (\nu' + \frac{1}{2}) \text{ and } x'' = (\nu'' + \frac{1}{2}).$$

33894.8

§ 4. THE EMISSION BANDS OF SnCl_2

The discharge through the vapours of SnCl_4 and SnCl_2 has been studied for a pressure of slightly less than 1 mm. of mercury, in each case with uncondensed discharge. Each discharge tube had a quartz window attached to one side of the end-on tube while the other side was fitted with a glass window. Simultaneous exposures were taken on the medium Hilger quartz spectrograph and a Hilger constant deviation glass spectrograph. In the case of both substances the two known band systems of SnCl were observed. In addition to these bands⁽¹⁷⁾ the spectrum of SnCl_2 vapour showed a set of narrow bands in the region $\lambda\lambda 4500$ to 4900 . These were absent in the spectrum of SnCl_4 vapour. We shall discuss these bands below. The regions of continuous emission given by SnCl_4 have their maxima at $\lambda\lambda 4245$, 3260 , 2580 , and $(2365?)$, while those of SnCl_2 are at $\lambda\lambda 4500$ and 3100 . The detailed

data on these continua are given in tables 11 and 12. The set of narrow bands observed in SnCl_2 have been measured on plates taken on Hilger constant deviation glass spectrograph giving an average dispersion of about 28 Å. per mm. in the region

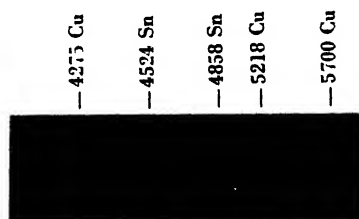
Table 11. SnCl_4

Long-wave-length limit			Maxima			Short-wave-length limit
Å.	Kcal./mol.	Electron-volts	Å.	Kcal.	Electron-volts	Å.
5100	55.5	2.5	4525	62.5	2.7	3910
3470	82.0	3.5	3260	87.0	3.6	3210
2620	108.0	4.7	2580	110.0	4.8	2520
2520	112.5	4.9	2365?	120.0	5.1	2400

Table 12. SnCl_2

Long-wave-length limit			Maxima			Short-wave-length limit
Å.	Kcal.	Electron-volts	Å.	Kcal.	Electron-volts	Å.
5200	55.2	2.4	4500	62.5	2.7	4000
3400	82.8	3.6	3100	92.0	4.0	3000

$\lambda 4500$ to 4900 . The bands are very faint and lie in the body of the first region of continuous emission. The bands are similar in appearance to those of group A bands of SiCl_2 system. They are rather broad and the direction of their degradation is not quite certain. Figure 5 is a reproduction of the plate. Table 13 gives the wave-lengths of the bands measured, together with the classification proposed.

Figure 5. Spectrogram of SnCl_2 bands.

These are the mean of two values obtained from two independent plates which are measured on the assumption that the bands are degraded towards longer waves. The average discrepancy between the two measurements is of the order of 1 Å. which introduces an error of about 3 cm^{-1} . A few bands below $\lambda 4549$ were visible on the plate to the naked eye, but could not be measured on the comparator.

The frequency of vibration connected with the ground state of the diatomic molecule SnCl is of the order of 351.4 cm^{-1} . Differences of this order of magnitude can be easily recognized in the present bands. The progressions in which the bands can be thus arranged give vibrational differences which, however, show marked

Table 13

Transitions, figure 7	λ_{air} (Å.)	ν_{air} (cm^{-1})	Classification		$\nu_{\text{obs}} - \nu_{\text{calc}}$
			$(\omega_a \omega_b)'$	$(\omega_a \omega_b)''$	
D	4796.4	20843	(0-0)'	(4-0)''	-5
F	4770.5	20956	(0-0)'	(2-2)''	+2
G	4744.5	21071	(0-0)'	(3-1)''	+4
C	4719.9	21181	(0-0)'	(3-0)''	-5
I	4691.2	21311	(0-0)'	(2-2)''	-2
F	4666.2	21425	(0-0)'	(2-1)''	-1
B	4639.6	21548	(0-0)'	(2-0)''	+3
H	4617.7	21650	(0-0)'	(1-2)''	0
E	4594.4	21760	(0-0)'	(1-1)''	-3
A	4568.1	21885	(0-0)'	(1-0)''	+3
K	4543.1	22005	(0-0)'	(0-2)''	0

discrepancy with those of the ground state of SnCl . This correspondence, without a close agreement, again indicates that the final level involved in these bands is probably the ground state of the triatomic molecule SnCl_2 . Furthermore, the ground level of SnCl is a $^2\Pi$ level with an electronic separation of 2360 cm^{-1} . If the final level of the bands under discussion were identical with the ground level of SnCl we should obtain a similar set of bands at about the same distance either on the long or short wave-length side of the bands. No such bands have been observed though looked for.

The analysis of the bands on the assumption that they are due to a triatomic molecule SnCl_2 , is displayed in table 14. In conformity with the analysis given for the group A bands of SiCl_2 , we again obtain frequencies ω_a and ω_b associated with two modes of vibration. We obtain three vibrational levels associated with one mode

Table 14*

—		—		22005
				(355)
21885	(125)	21760	(110)	21650
(337)		(335)		(339)
21548	(123)	21425	(114)	21311
(367)		(354)		(355)
21181	(110)	21071	(115)	20956
(338)				
20843		—		—

of vibration and two levels with the other in the ground state of the molecule. The excited state does not exhibit any vibrational levels, exactly as in the group A bands of SiCl_2 . The breadth of the bands again indicates the possibility that the vibrational frequencies associated with this excited level are of an order of magnitude such that the differences between these and the frequencies in the ground state result in bands which differ very slightly in wave-lengths, as in the case of group A

* The actual vibrational quantum numbers of the transitions giving these bands are given in table 13.

bands of SiCl_2 . Figure 6 shows a reproduced microphotometer curve showing at least three components in each band. The $(\text{o-o})'-(\text{o-o})''$ band is too faint to be measured, being on the shorter wave side of the last band measured on the comparator. Figure 7 is a diagrammatic representation of the transitions observed.

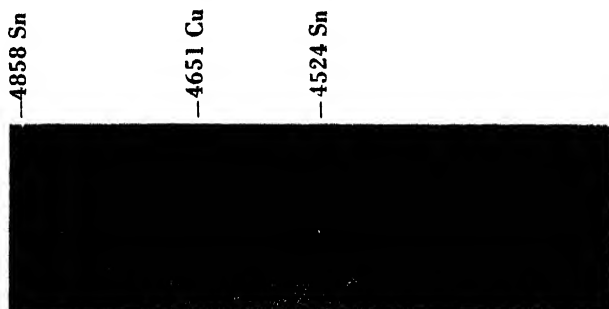


Figure 6. Microphotometer record of SnCl_2 bands.

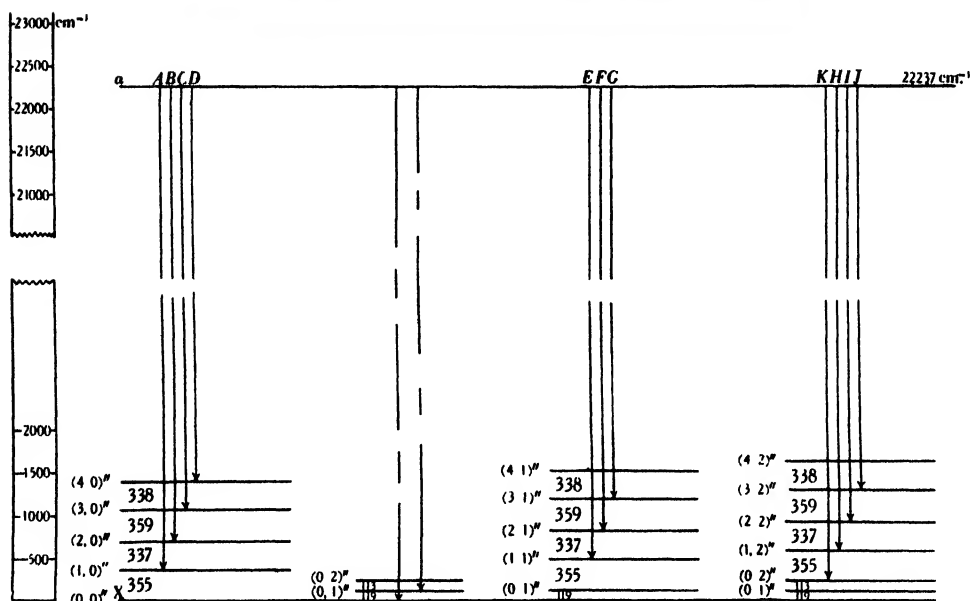


Figure 7. Simple and multiple transitions of SnCl_2 bands.

With the same notation as is used before for SiCl_2 , the $\Delta G''(v_a)$ and $\Delta G''(v_b)$ values are given in tables 15 and 16.

Table 15. $\Delta G''(v_a)$ values for ω_a mode of vibration

0-1	1-2	2-3	3-4
355	337 335 339	367 354 355	338
Mean 355	337	359	338

Table 16. $\Delta G''(v_b)$ values for ω_b mode of vibration

0-1	1-2
125	110
123	114
110	115
Mean 119.3	113.0

The $\Delta G''(v_a)$ values are irregular and an evaluation of the anharmonic factor is not possible. For $\Delta G''(v_b)$ we have only two values which decrease regularly and which give $\omega x = 3$. ω_a is therefore $= 355 \text{ cm}^{-1}$ and $\omega_b = 122 \text{ cm}^{-1}$.

Exactly as in SiCl_2 , we identify ω_a'' as the symmetric valence vibration, the value of 355 being near to $\omega'' = 351.4$ of SnCl and the valence vibration of $\text{SnCl}_4^{(7)}$ of 366 cm^{-1} . The frequency $\omega_b'' = 122$ becomes the deforming vibration, being smaller than half of ω_a'' . Applying the same remarks that we have offered for SiCl_2 , we are led to the conclusion that this level of SnCl_2 is also the ground state of the molecule, and that the molecule is non-linear. The close proximity of $\omega_b'' = 122$ with the two deforming frequencies $^3\delta$ and $^2\delta$ of SnCl_4 , which are 134 cm^{-1} and 104 cm^{-1} respectively, further indicates that ω_b'' represents the frequencies connected with the deforming mode of vibration. The antisymmetric valence vibration has not been observed for SnCl_2 . In this respect also the behaviour of the molecule is completely analogous to that of SiCl_2 and is in agreement with Herzberg and Teller's theory⁽¹⁶⁾.

An extrapolation of the bond energy of SnCl_2 from the band spectroscopical data is out of question, but the atomic heat of formation has been calculated recently⁽¹⁰⁾ as $D(\text{SnCl}_2) = 180.8$ and $D(\text{SnCl}_4) = 300.5 \text{ kcal./mol.}$ This gives 3.8 e.v. for the bond energy $D_B(\text{Sn}^{\text{II}}-\text{Cl})$ and for $D_B(\text{Sn}^{\text{IV}}-\text{Cl}) = 3.9 \text{ e.v.}$ obtains if the excitation energy of the ^5S term of Sn is estimated to about 2.4 e.v.

The main results of these investigations are displayed in table 17. Some of the figures are not very accurate, both of spectroscopic as well as of thermochemical origin. But the table shows certain regularities which appear to be real. The excitation energy of the triatomic molecule with an even number of electrons is less than that of the odd numbered corresponding diatomic one. The symmetric valence vibration of both are almost identical, those of the corresponding higher polyatomic chlorides are not far off. Similarly the bond energies of both the former ones appear to be very nearly related. For the higher chloride we expect a higher bond energy because the electronic configuration undergoes a sudden change by the s^2 group being fissured, probably the internuclear distance becomes smaller and the molecular refractivities in such cases show a smaller polarizability. A tendency in this direction is certainly present among the tin chlorides but is less marked among those of silicon. One feature, however, cannot be understood at present, i.e. the valence vibration of SiCl_4 is smaller than those of SiCl and SiCl_2 , whereas among the tin chlorides just the opposite happens. Summarizing, we might say that these spectra again indicate a close relation between the bonds of

these corresponding molecules and therefore a rather strong localization of the bonds.

Table 17

	SiCl	SiCl ₂	SiCl ₄	SnCl	SnCl ₂	SnCl ₄
Excitation energy (cm ⁻¹)	34136 41235 45006	28295 29952 —	— — —	28939 33622 —	22237 — —	— — —
Symmetric valence vibration. Ground state (cm ⁻¹)	531	540	425	351	355	366
Deforming vibration. Ground state (cm ⁻¹)	—	248	221, 151	—	122	134, 104
Bond energy (e.v.)	4.0*	4.0†	4.0†	3.5*	3.8†	3.9†

* Band spectra.

† Thermochemical value.

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THE ACOUSTICAL CONDUCTIVITY OF ORIFICES

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ABSTRACT. Measurements made on the acoustical conductivities of the following orifices are described: (1) At the junctions between two tubes in series and two tubes in parallel; (2) Multiple thin orifices in parallel; (3) Long orifices forming constrictions in a tube and long orifices terminating a tube. Equations are given for calculating the conductivities of orifices associated with various acoustical structures. A method is described, of determining the shapes of acoustical wave-fronts near any constriction in a cylindrical tube, and results are given for thin circular orifices.

§ 1. INTRODUCTION

THE conductivity of an orifice is defined as the constant of proportionality between the difference in velocity-potential on each side of the orifice and the resulting volume velocity. It is called conductivity because of its analogue in electricity, the reciprocal of resistance. The acoustical impedance of an orifice can be shown to be almost a pure reactance $i\rho\omega/K$, where ρ is the density of the medium, ω is the pulsance, and K is the conductivity. When the orifice is of very small diameter, viscous effects may introduce a resistance term into the impedance, but in all the orifices to be considered here the reactance term predominates and hence the resistance may be neglected.

The method of experiment has been described previously⁽¹⁾ but the theory may be briefly recapitulated without any of the practical details. The impedance Z_1 at any point in a cylindrical tube is given by

$$Z_1 = \frac{i \cos kl_1 Z_2 - R \sin kl_1}{-R^{-1} \sin kl_1 Z_2 - i \cos kl_1} \quad \dots\dots(1),$$

where Z_2 represents the terminating impedance, $i_2 = -1$, $k = \omega/c = 2\pi/\lambda$, where c and λ are the velocity and wave-length of the sound respectively, $R = \rho c/S$, S is the area of cross-section of the tube, and l_1 is the distance from the point P to the terminating impedance Z_2 .

If, now, Z'_2 is the terminating impedance at the other end of the tube, distant l'_1 from P , an expression similar to (1) may be written down for the impedance at P . The two expressions are identical, but a distinction is made in the nomenclature in order to distinguish between the impedance at the point due to one end of the tube and that due to the other. The loudspeaker, which drives the system, forms part of the impedance Z'_2 , the other part being a branch tube with which the impedance can be varied. Z_1 is made zero by making Z_2 a rigid end and l_1 equal to $\frac{1}{2}n\lambda$, where n is an odd integer. A microphone placed at P will record

minimum sound but not necessarily silence. Silence can be obtained, however, by adjusting Z'_2 . The impedance at P and hence the acoustic pressure must be zero. Putting $Z_1 = 0$ in expression (1) we have

$$0 = i \cos kl_1 Z_2 - R \sin kl_1$$

or

$$Z_2 = -ipc/S_1 \tan 2\pi l_1/\lambda \quad \dots\dots(2).$$

Hence Z_2 is given in terms of l_1 .

By applying this method, the conductivities of thin orifices forming constrictions in a tube were found to be represented by the formula

$$C = \frac{0.787 d}{\left(1 - \frac{d}{D}\right)^{1.895}} \quad \dots\dots(3),$$

where d and D are the diameters of the orifice and tube respectively and C is the conductivity in an infinitely thin sheet. When the orifices formed terminations to the tube the conductivity was given by

$$C = d \left(1 + \frac{d}{D}\right)^{1.19} \quad \dots\dots(4).$$

§ 2. WAVE-SHAPES NEAR AN ORIFICE IN A TUBE

One of the effects noticed in the first set of experiments on constrictions in a tube was that the measured value of the conductivities depended upon the nearness of the pressure tube to the orifice. When the tube was remote from any particular orifice a constant value of conductivity was obtained for that orifice, but when the tube was within 1 or 2 cm. of the orifice abnormally high values were obtained. The effect is shown in figure 5 of the paper quoted. It was thought to be due to the distortion of the wave-fronts in the tube as a result of the presence of the orifice.

The actual shapes of the waves were determined as follows: with the opening of the pressure tube on the axis of the main tube, distance pieces were inserted in the tube whereby the orifice was moved in steps of 0.159 cm. away from the pressure tube, i.e. l_1 was increased in steps of 0.159 cm. For each setting of l_1 the length of tube l_2 behind the orifice was adjusted by means of a piston until silence was obtained. The pressure tube was then displaced from the axis, and again measurements of l_2 were made while l_1 was varied. The experiments were performed for radial displacements of the pressure tube of 0.25, 0.5, 1.0, 1.5, 2.0 and 2.3 cm. from the axis. Curves were drawn, figure 1 (*a, b, c, d*), showing the relationship between l_2 and the radial displacement r , for the various values of l_1 shown alongside the curves.

The decrease in l_2 shown where the pressure tube is actually in the orifice, so that the radial displacement is zero and $l_1 = 0$, is due to effective reduction in area causing decreased conductivity at the orifice. It will be seen that this effect is greatest in the smallest orifice, where the pressure tube occupies a relatively large proportion of the opening. The dotted lines show the probable value of l_2 .

Consider a line on figure 1 (b) corresponding to a constant value of l_2 of 7.3 cm. It intersects lines of constant l_1 at points u , v , w . This may be interpreted by

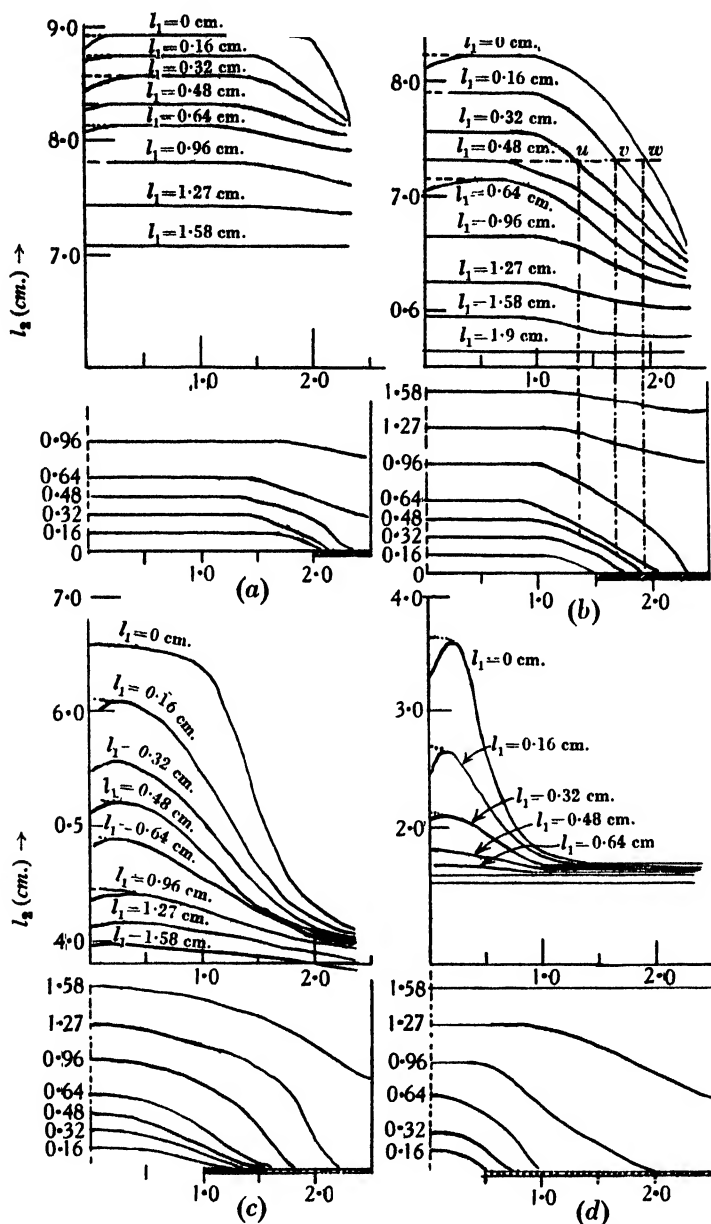


Figure 1. Relation between l_2 (cm.) and the radial displacement r (cm.).
Diameter of orifice: (a) 4.0 cm.; (b) 3.0 cm.; (c) 2.0 cm.; (d) 1.0 cm.

assuming that the experiment had been performed by keeping the length of tube behind the orifice constant at 7.3 cm. and obtaining silence in the microphone by adjusting the length of tube in front of the microphone. Silence would have been

obtained at the values of l_1 and r given by the points u , v , and w on the graph. Now if l_1 and r are plotted the contours of the equipressure or equipotential surfaces are obtained. The lower graph of figure 1 (*b*) shows these surfaces, the accentuated portion of the radial displacement axis denoting the surrounds of the orifice. Radial displacements of the pressure tube were only made on one side of the axis, since it could be assumed that conditions were symmetrical with regard to the latter.

Wave shapes are shown for circular orifices of 1.0, 2.0, 3.0 and 4.0 cm. in a tube 5.08 cm. in diameter. It is seen that for the largest orifice (4.0 cm.) the plane components of the velocity-potential predominate, the non-planar wave-front being confined to a small region in the neighbourhood of the edges. Again, for the smallest orifice (1.0 cm.) the disturbed region is at the axis of the tube, while the plane components persist near the walls. For the 3.0 and 2.0-cm. orifices the distorted wave-fronts affect practically the whole of the section of the tube and persist to a greater distance from the orifices. These results verify those described in the previous paper and illustrated in figure 5 on p. 778 thereof. This method is applicable to the measurement of the shapes of acoustical wave-fronts near any apparatus connected in a tube.

§ 3. MULTIPLE ORIFICES TERMINATING A TUBE

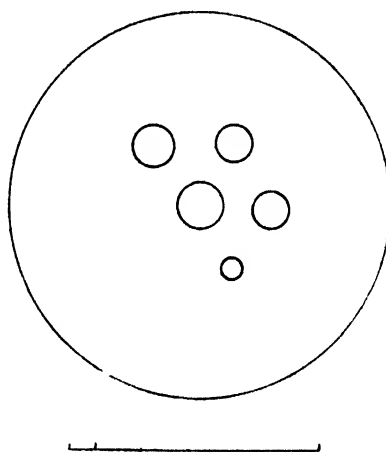
The effect of two or more orifices terminating a tube was next investigated. For this purpose, a disk 0.159 cm. thick and 7.62 cm. in diameter was bored with holes from 0.1 to 0.9 cm. in diameter in steps of 0.1 cm., 0.5 cm. being omitted. The centres of the holes were equally spaced on a circle round the largest orifice. The conductivity of each hole was measured separately and then various combinations of orifices were used. Table 1 gives a summary of the results obtained. The measured value of the conductivity of two or more orifices is, in every case, less than the sum of the conductivities measured separately. By reference to

Table 1. Conductivities of orifices in parallel at the end of a tube, arranged as in figure 2

Arrangement of orifices, and diameters (cm.)	K		Ratio of measured K to calculated K
	Measured	Calculated	
0.4	0.40	—	—
0.60	0.62	—	—
0.70	0.76	—	—
0.80	0.86	—	—
0.9	0.94	—	—
0.80, 0.9	1.56	1.80	0.87
0.7, 0.8, 0.9	1.86	2.56	0.72
0.6, 0.7, 0.8, 0.9	2.31	3.28	0.73
0.4, 0.6, 0.7, 0.8, 0.9	2.50	3.58	0.70
0.9, 0.7	1.49	1.70	0.88
0.9, 0.6	1.36	1.56	0.87
0.8, 0.6	1.33	1.48	0.90
0.8, 0.70	1.35	1.62	0.83
0.7, 0.6	1.14	1.38	0.83

figure 2, which shows the relative positions of the orifices, it is noticeable that the orifices 0.8 and 0.6 cm. in diameter show the greatest percentage ratio between the measured and additive values. They are also the farthest apart. The 0.9 and 0.7, the 0.9 and 0.6, and the 0.9 and 0.8-cm. orifices have the same spacing and show a ratio of 87 per cent, while the combinations of the 0.8 and 0.7 and the 0.7 and 0.6 orifices, being less distant, show a lower ratio.

The results show, therefore, that the proximity of the orifices has the effect of reducing the ratio of the measured conductivity to the sum of the separate conductivities. The ratio also decreases with the number of orifices arranged in parallel. It was impossible, in a tube 5.08 cm. in diameter, to space the orifices sufficiently far apart to enable a numerical relation between the spacing of two similar orifices and their conductivity to be determined. Nor was it convenient to determine the effect of a large number of holes of equal diameter, for if the orifices were too near to the walls there would be interference due to the wall, while if the orifices were made too small the resistance would not be negligible and hence the results would not be reliable. It appears, therefore, that the actual conductivity of a set of holes forming a constriction in a tube or terminating a tube must be determined separately in each individual case. The results given do indicate, however, the order of the reduction in conductivity which is produced when multiple orifices are used.



5 cm.
Figure 2.

§ 4. ORIFICES IN PARALLEL WITH THE MAIN TUBE

Experiments were now performed on orifices bored in the walls of the main tube. The orifices were therefore effectively in parallel with the main tube, since a wave propagated in the tube could be transmitted either along it or through an orifice. The impedance Z_2 in equation (1) is now the effective impedance of a pipe and the orifice in parallel. The case is treated in the appendix, equation (3a), where it is shown that the conductivity can be calculated from the relation

$$\frac{\lambda K}{2\pi S} = \tan \frac{2\pi l_2}{\lambda} - \cot \frac{2\pi l_1}{\lambda} \quad \dots\dots(3a).$$

Measurements were made on six orifices 0.6–2.52 cm. in diameter at a frequency corresponding to a half-wave-length of 15.73 cm. at 21.2° C. Several values of l_1 were used and then $\tan (2\pi l_2/\lambda)$ was plotted against $\cot (2\pi l_1/\lambda)$, figure 3. The intercepts of the resulting straight lines on the axes were given by $\lambda K/2\pi S_1$, from which K was calculated for each orifice. The measured value was reduced to the conductance of a similar orifice in a thin sheet by the relation

$$\frac{1}{K} = \frac{1}{C} + \frac{L}{A} \quad \dots\dots(5).$$

Experimental points are indicated in figure 4, which also shows the conductivities of orifices forming constrictions, curve (1), and of orifices terminating a tube, curve (2), reproduced from the previous paper. It is seen that the points agree closely with curve (2). The agreement is not so good for the larger orifices,

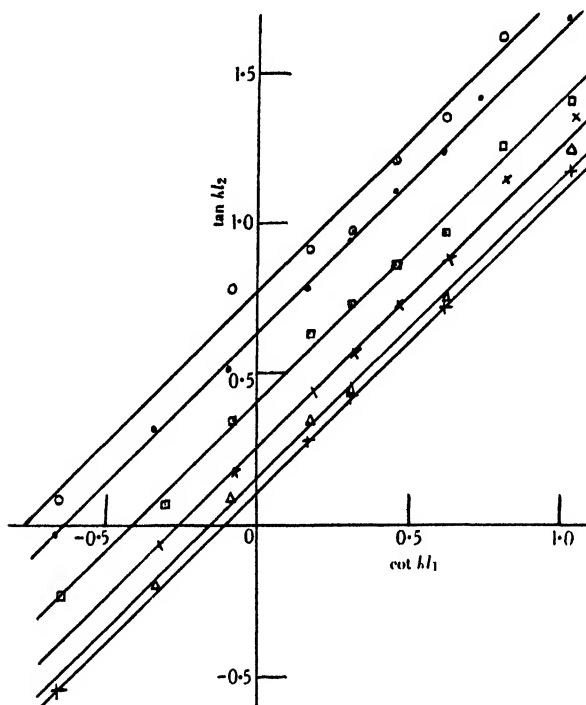


Figure 3. Orifices in parallel in a tube; $k = 2\pi/\lambda$. Diameter of orifice (cm.): \odot , 2.52; \bullet , 2.06; \square , 1.50; \times , 1.06; \triangle , 0.80; $+$, 0.60.

and this may be due to the fact that the orifices were not plane in section but were bored directly out of the walls of the tube. Another difference in the conditions is that instead of the wave arriving in the same phase all over the orifice, as it does in a terminating impedance, there is a slight difference in phase from one end to the other. This is small except in the larger orifices. Lower values for the conductivities may be expected, too, because the orifice is practically free on each side and hence approaches the Rayleigh condition.

§ 5. CONDUCTIVITIES AT THE JUNCTION OF TWO TUBES OF DIFFERENT DIAMETERS

The problem of the impedance at the junction of two tubes was next investigated, with the tubes first in series and then in parallel with the main tube. The tubes to be measured were fitted with massive pistons similar to that in the main tube, and each subsidiary tube was soldered to a flange which could be easily attached to the connecting piece and so form an extension to the main tube. The

structure thus consisted of an orifice in series with a closed tube and its impedance was therefore given by

$$\frac{i\rho\omega}{K} - \frac{i\rho c}{S_2} \cot \frac{2\pi l_2}{\lambda},$$

where S_2 is the area of cross-section of the small tube and l_2 is the distance from the piston to the orifice. When silence was obtained in the headphones, the conductivity could be calculated from the relation

$$\frac{2\pi S_1}{\lambda K} = \frac{S_1}{S_2} \cot \frac{2\pi l_2}{\lambda} - \tan \frac{2\pi l_1}{\lambda} \quad \dots\dots(1a),$$

see equation (1a) of the appendix.

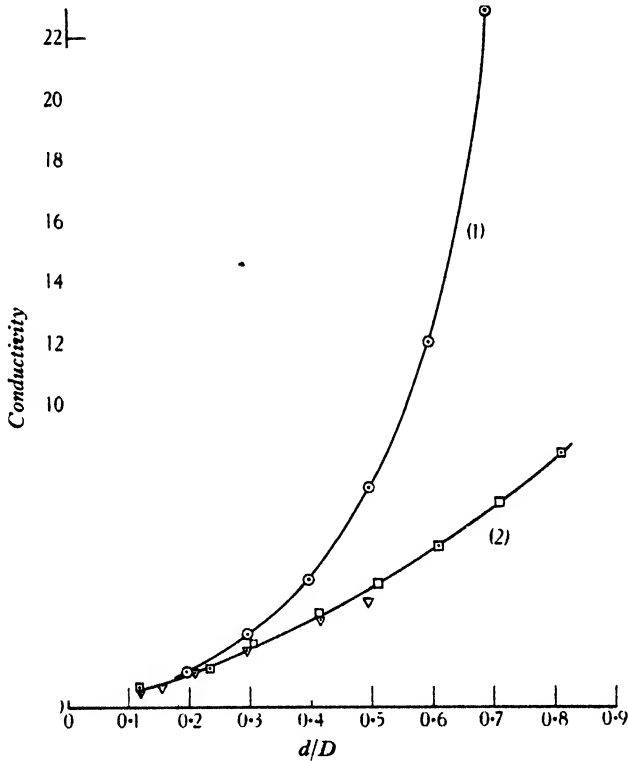


Figure 4. \odot , orifices forming constrictions in a tube; \square , orifices terminating a tube; ∇ , orifices in the tube walls.

The small tube was placed about half a wave-length from the pressure tube, in order to avoid the region of nonplanar wave-shapes and also to avoid large values of $\cot (2\pi l_2/\lambda)$ and $\tan (2\pi l_1/\lambda)$ which would be obtained if the junction were in the neighbourhood of a node. In this case $(S_1/S_2) \cot (2\pi l_2/\lambda)$ was plotted against $\tan (2\pi l_1/\lambda)$ as shown in figure 5. K was calculated from the intercepts. The results are also plotted against the ratio of the diameter of the smaller tube to that of the larger in figure 6. The curve is found to be represented by the formula

$$C = \frac{2.0d}{(1-d/D)^{1.448}} \quad \dots\dots(6).$$

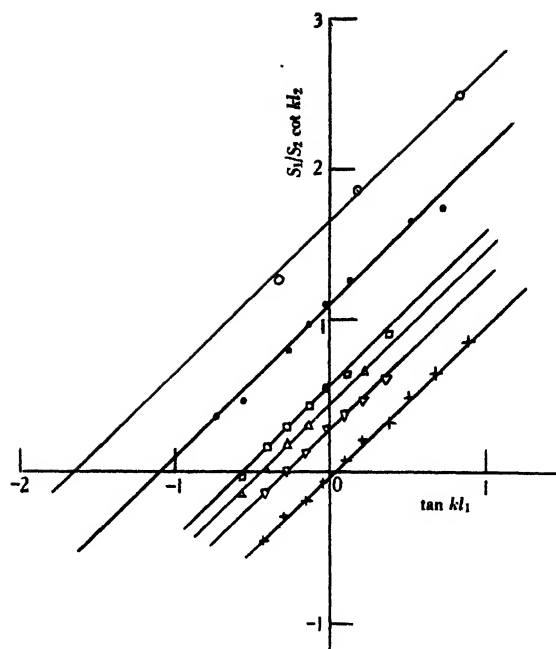


Figure 5. Tubes in series; $k=2\pi/\lambda$. Diameter of tube (cm.): \circ 0.91; \bullet , 1.24; \square , 1.86; \triangle , 2.17; ∇ , 2.48; $+$, 5.98.

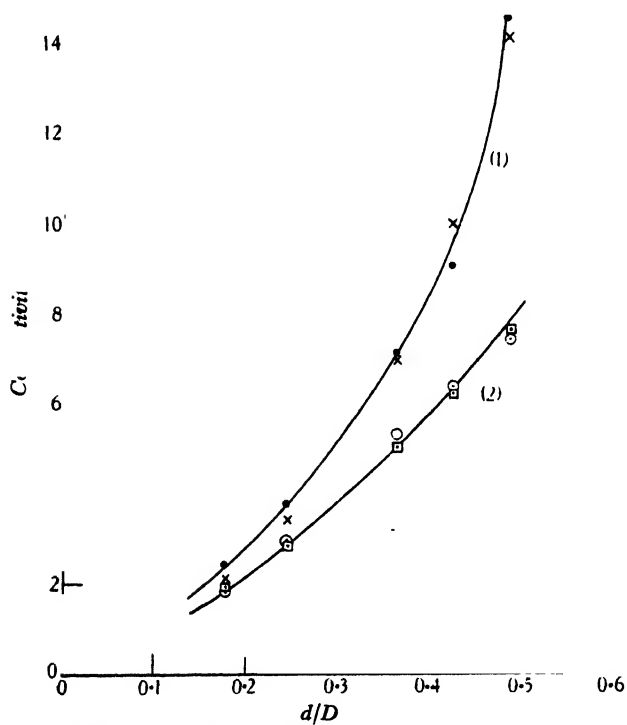


Figure 6. (1) tubes in series; (2) tubes in parallel. \times points representing twice the conductivity of thin orifices in series; \square points representing twice the conductivity of thin orifices in parallel.

Values calculated from the above expression are placed in column 5, table 2, and in the same table are shown the conductivities of thin constrictive orifices of the same diameter as the various tubes taken from curve (3), figure 4. The ratio of the conductivity at the junction to that for a thin constriction is about 2.1. This confirms a result previously obtained by A. E. Bate⁽²⁾ that the conductivity of a single face should be twice that of an orifice having two sides.

Table 2. Conductivities at the junction between two tubes.

D , 5.08 cm.; $\lambda/2$, 15.84 cm.; temperature, 21° C.

Diameter d of tube (cm.)	d/D	Inter- cepts from figure 5	Conductivities			Ratio of K for tube to K for orifice
			Measured	Calculated from equation (6)	For orifice from curve (3) of figure 4	
2.48	0.488	0.285	14.0	13.1	7.1	1.98
2.17	0.427	0.435	9.2	9.7	5.0	1.85
1.86	0.366	0.555	7.24	7.20	3.5	2.07
1.24	0.244	1.09	3.70	3.72	1.7	2.18
0.91	0.179	1.65	2.43	2.42	1.05	2.43
5.98	1.17	0.03	134	158	—	—

A. E. Bate has also investigated experimentally the effect at the junction of two tubes. His experiments were performed on organ pipes having extensions of different diameters, and with these he verified a relation given by Aldis and stated in the appendix. The organ pipe was 5.4 cm. diameter and had attached a large tube 7.6 cm. in diameter which gave a ratio d/D of 1/0.71. He determined the position of an antinode in the organ pipe, sounding a particular frequency alone, and then attached the large tube and adjusted the lengths of the organ pipe and extension pipe until the same frequency was obtained. He assumed that the antinode remained at its previous position, and from the remaining length of the main pipe and the length of the extension pipe he calculated the ratio d/D from Aldis's formula. His results show good agreement (0.75, 0.78, 0.73, 0.71, 0.70, 0.71, 0.73) but the effect at the junction was neglected.

There is no reason to suppose that the conductivity at the junction between two tubes of different area should be greater in one direction than another, so that equation (6) should be applicable when d and D are interchanged; the junction may be regarded as composed of a tube 7.6 cm. forming the main tube and an end tube 5.4 cm. in diameter. Therefore $d/D = 0.71$. With this assumption $K = 65$ and the term $2\pi S_1/\lambda K$, by which equation (1a) differs from the Aldis equation (2a), amounts to only 0.048. The two expressions therefore differ from each other only slightly when d/D is large. Where d/D is small, however, there may be considerable differences. The Aldis equation assumes that the corrected lengths of the respective tubes are used.

The meaning of end correction in such a case is very vague because when the

diameters of the tubes are not too dissimilar each may be considered an approximately open pipe and hence each would require an end correction. The total end correction can be determined easily by experiment, but the proportion of end correction to be applied to each tube would be very difficult to assess.

It seems preferable therefore to consider the junction as a separate entity having a conductivity from which the impedance can be calculated, and to use the geometrical lengths of the two associated tubes for calculating the impedance of the structure embodying the junction.

§ 6. TUBES IN PARALLEL WITH THE MAIN TUBE

In order to attach tubes in parallel with the main tube a short length of brass tube 5.08 cm. in diameter was fitted with flanges by means of which it could be connected in the main tube. It had a platform screwed to it so that the branch tubes could be attached. A hole was bored right through the centre of the platform and the wall of the main tube towards the axis. Owing to the thickness of the platform and the curvature of the main tube there was a region which had to be filled with plasticene to form the junction to the branch. The actual opening of the branch tube into the main tube thus conformed to the curvature of the main tube. In equation (4a) of the appendix it is shown that the conductivity of the orifice at the junction of the two tubes is given by

$$\frac{2\pi S_1}{\lambda K} = \frac{S_1}{S_3} \cot \frac{2\pi l_3}{\lambda} - \frac{1}{\tan(2\pi l_2/\lambda) - \cot(2\pi l_1/\lambda)} \quad \dots\dots(4a),$$

where S_1 and S_3 are the areas of cross-section of the main tube and branch respectively, l_1 is the length in the main tube from the pressure tube to the centre of the branch, l_2 the length in the main tube from the centre of the branch to the rigid piston, and l_3 is the length of the branch tube. The procedure was to keep l_1 constant and increase l_2 in steps of 1.0 cm., l_3 being adjusted at each step to give silence in the headphones. An alternative method was to vary l_3 in steps of 1.0 cm. and adjust l_2 to give a minimum. Both methods were tried but it was found that a more definite minimum was given by the first method. Figure 7 shows the result of plotting $(S_1/S_3) \cot(2\pi l_3/\lambda)$ against $(\tan 2\pi l_2/\lambda - \cot 2\pi l_1/\lambda)^{-1}$, from which the intercepts $2\pi K S_1/\lambda$ were obtained.

There was some doubt as to the length to be measured for l_3 , for the length measured along the axis of the branch tube to the wall of the main tube was shorter than that measured along the wall of the branch tube to the wall of the main tube on a section perpendicular to the main tube axis and lying along the branch tube axis. The results were calculated for both methods of measurement and it was found that the latter gave better agreement with twice the conductivity of orifices of the same diameter in parallel, since this relationship was found to hold between these orifices and tubes in series with the main tube. The conductances are plotted in curve (2) of figure 6, the measured points being marked with a dot and circle while points marked with a square represent twice the conductivity of corresponding thin orifices in parallel as obtained from curve (2) of figure 4. W. P.

Mason⁽³⁾ in his treatment of acoustical wave filters specifies that the length of a branch tube should be measured from the centre of the main tube, but this view is not borne out by the above results. The subject requires further investigation.

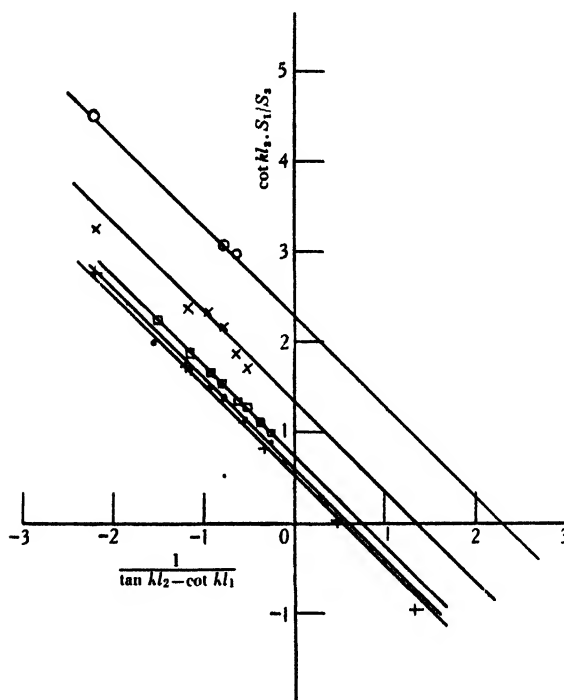


Figure 7. Tubes in parallel; $k = 2\pi/\lambda$. Diameter of tube in parallel (cm.): \circ , 0.91; \times , 1.24; \square , 1.86; \bullet , 2.17; $+$, 2.48.

It should be possible to obtain the shape of the wave-fronts in the neighbourhood of the junction by the method described in § 2. It would probably be found that in the case of ratios of d/D greater than about 0.5 the disturbance of the wave-fronts extends right across the main conduit, in which case it would be very difficult to predict an end correction. It seems preferable therefore to calculate the conductivity from the geometrical lengths of the tubes used.

§ 7. LONG ORIFICES AS CONSTRICTIONS IN A TUBE

The same method of experiment was used to measure the conductivities of long orifices or short tubes placed as constrictions in or at the end of a tube. A set of disks of thickness 0.3175, 0.635, 0.953 and 1.25 cm. was used, and all were bored at the centre with a hole of the same diameter. By using each disk separately and then in various combinations the length of the orifice could be increased to 3.175 cm. in steps of 0.3175 cm. The conductivity could be calculated from equation (8a). In order to prevent inaccurate results due to non-planar wave-fronts, the orifice was removed to distances in the neighbourhood of $\lambda/2$ from the pressure tube.

Orifices of 1.24, 1.89 and 2.52 cm. were measured at a frequency corresponding to a wave-length of 36.26 cm. at a temperature of 23° c., and the results are plotted in figure 8, each point on the graph being the mean of from six to ten separate measurements. It is evident from the graph that the length of the orifice has a profound effect on its conductivity, and to test the validity of the equation

$$\frac{1}{K} = \frac{1}{C} + \frac{L}{A}$$

for long orifices the value for a thin orifice of the same diameter was taken from figure 4 and substituted for C in the above equation. Then when A , the area of

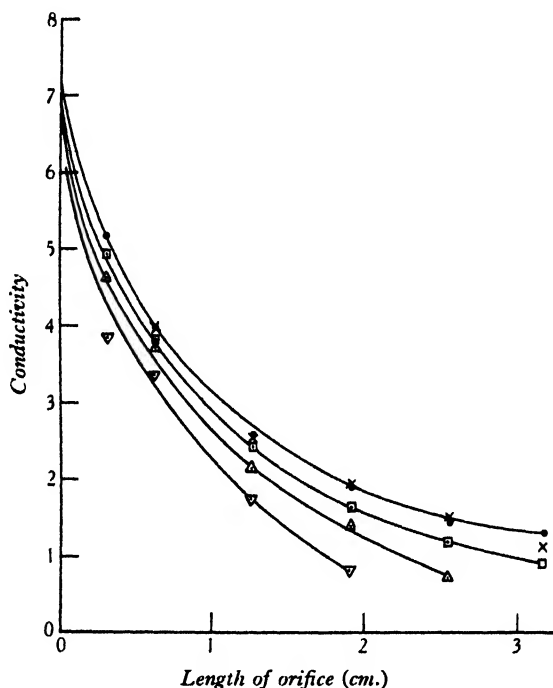


Figure 8. Orifices in tubes; variation of conductivity with length and frequency.
Half-wave-length (cm.): ●, 18.13; ×, 13.35; □, 10.56; △, 7.98; ▽, 6.15.

cross-section, and K , the measured conductivity, were known, a length L could be calculated which would be the effective length of the orifice. The ratio of the effective length to the measured length of the largest orifice is given in table 3. The experiments on the largest orifice were repeated at several different frequencies, and the results are shown in figure 9. As at the lowest frequency, the ratio of the effective length to the measured length was calculated, and this also is shown in table 3. There it is shown that the ratio is unity for an orifice whose length is equal to the diameter up to a frequency of about 1200 c./sec. when the diameter of the orifice is half the diameter of the tube. If the length is increased further, or the frequency raised, then the effective length is much larger than the actual length.

On theoretical grounds one would expect that, at any particular frequency, as the length increased the medium inside the orifice would cease to move bodily, as the idea of conductivity implies, but begin to take up part of the wave-motion.

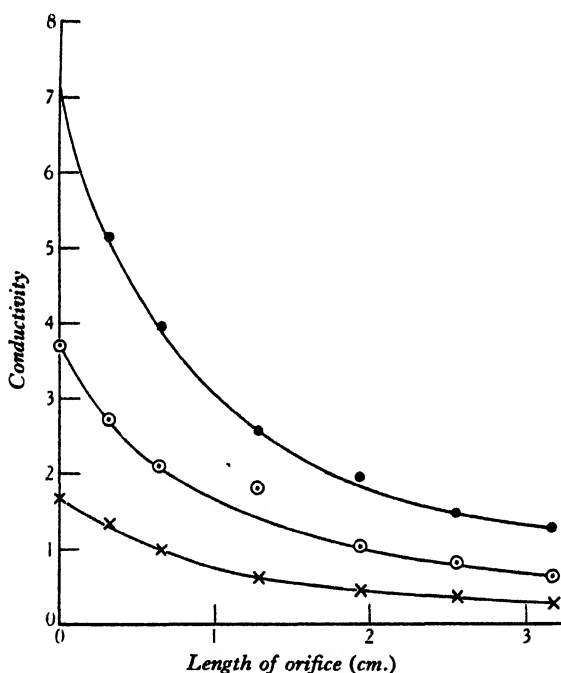


Figure 9. Orifice in tube; variation of conductivity with length.
Diameter of orifice (cm.): ●, 2.54; ○, 1.89; ×, 1.24.

The orifice would then need to be considered as a short length of open tube with a separate orifice at each end. This case has been examined mathematically in the appendix, and a rather complicated expression, equation (7a), results. For the short lengths of tube under consideration it is sufficiently accurate to consider their lengths to be increased in the ratios given in table 3.

Table 3

Half-wave-length (cm.)	18.13	13.85	10.56	7.98	6.15
Length of orifice (cm.)	Ratio of effective length to measured length				
0.32	1.01	1.01	0.98	1.14	1.37
0.635	1.01	1.01	1.00	1.20	1.47
1.27	1.00	1.00	1.11	1.28	1.82
1.91	1.00	1.00	1.21	1.53	2.81
2.54	1.00	1.04	1.31	1.88	—
3.18	1.00	1.13	1.43	—	—

Diameter of orifice, 2.52 cm.; diameter of tube, 5.08 cm.

A tube which could be considered short at one wave-length would need to be considered long at a shorter wave-length. The limiting frequency at which the

orifice may be considered short enough for equation (5) to apply without modification is rather indefinite, but these results indicate that a ratio (length of orifice)/(wave-length) of about 0.07 represents the upper limit.

Similar measurements were made on an orifice 2.5 cm. in diameter, of a length increasing to 2.54 cm., and terminating a tube at a frequency corresponding to a wave-length of 36.26 cm. It was found that equation (5) could be used for reducing the conductance to that of a thin sheet within the limits that are applicable for the orifices in a tube.

§ 8. SHORT TUBES

In order to test the supposition that a long orifice can be considered as an open tube with orifices at each end, measurements were made on constrictions 2.66 cm. in diameter and of lengths increasing from 1.0 to 16 cm. in steps of 1 cm., and at a frequency corresponding to a wave-length of 16.51 cm. at a temperature of 24° C. As is shown in the appendix, equation (7a), the tubes could be considered as consisting of a single tube with junctions having conductivity K at each end. Since the structure was symmetrical the conductivities of the orifices at each end should be the same, but a distinction between them is made in equation (7a) so that it might be possible to verify the assumption by measurement. The conductivity at the junction nearest the pressure tube was obtained from curve (1) of figure 6, and the conductivity at the remote junction was calculated by substituting the measured lengths of the tubes when a minimum sound was obtained from the microphone.

It was found that (1) the measured conductivity was unreliable when the length of the constriction was small; (2) the measured conductivity was also unreliable when the length of the constriction was approximately one quarter wave-length, and (3) a mean of conductivities measured on six constrictions of lengths 10 to 16 cm. resulted in a figure 12 being obtained instead of 15 from curve (1) of figure 6.

The agreement in finding (3) may be considered to be as satisfactory as the method will allow, as equation (7a) involves the tangents of three angles one of which $2\pi l_3/\lambda$ could be only approximate as the position of minimum sound intensity was not so clearly defined as in the previous experiments. The method of calculation was not strictly applicable to finding (1), for then the constriction could be treated as a short orifice and a correction applied for length as given by equation (5). In the second finding, however, the method of measurement was inaccurate because the length of the constriction gave rise to angles $2\pi l_1/\lambda$ and $2\pi l_3/\lambda$ in which the tangents were varying very rapidly.

The same tubes were then made to terminate the main tube. As for the long constrictions, the orifice was treated as a length of tube having an orifice at each end, the nearer orifice being at the junction between the main tube and the smaller tube while that at the remote end was the open end of the tube fitted with a baffle 5 ft. square. The case is treated mathematically in the appendix, and the result is given in equation (10a). Again the minimum was not so sharp as with the shorter orifices and hence the results are not so consistent. The measured conductivity at the remote end of the orifice tube was found to be 5.5 for the mean of seven lengths

of tube from 10 to 16 cm., instead of 6.0 calculated from equation (4). For lengths of tube about one-quarter of a wave-length long the measurements were inaccurate. For shorter lengths of tube they could be considered as having been made on a single orifice and the usual correction could be applied.

APPENDIX. EVALUATION OF EQUATION (2)

The structures to be dealt with can be considered as made up of orifices together with open and closed cylindrical tubes. The impedances of these basic structures can be readily obtained from equation (1). Thus the impedance of an orifice is given by $i\rho\omega/K$, that of a closed tube by $-(i\rho c/S) \cot(2\pi l/\lambda)$, and that of an open tube by $(i\rho c/S) \tan(2\pi l/\lambda)$, where ρ is the density of the medium and c and λ are respectively the velocity of sound and wave-length in the medium, while K is the conductivity, ω the pulsance, l the length of tube considered, and S the area of cross-section.

Let P , figure 10(a), represent a point in the experimental-acoustical system. Then the condition for zero acoustical pressure at P is given by

$$Z_2 = -(i\rho c/S_1) \tan 2\pi l_1/\lambda \quad \dots\dots(2),$$

where Z_2 is the terminating impedance.

The first structure considered consists of a closed tube concentric with a larger tube, figure 10(b). In this case

$$Z_2 = i\rho\omega/K - (i\rho c/S_2) \cot(2\pi l_2/\lambda),$$

where K is the conductivity at the junction. Substituting in equation (2) we have

$$i\rho\omega/K - (i\rho c/S_2) \cot(2\pi l_2/\lambda) = -(i\rho c/S_1) \tan(2\pi l_1/\lambda),$$

$$\text{from which} \quad 2\pi S_1/\lambda K = (S_1/S_2) \cot(2\pi l_2/\lambda) - \tan(2\pi l_1/\lambda) \quad \dots\dots(1a).$$

If the impedance at the junction is neglected, then equation (1a) becomes

$$S_1/S_2 = \tan(2\pi l_1/\lambda) \tan(2\pi l_2/\lambda) \quad \dots\dots(2a).$$

Here l_1 and l_2 are supposed to contain the end corrections. This equation was given by Aldis⁽⁴⁾.

Orifice in parallel with the tube, figure 10(c). In this case Z_2 must be considered as the effective impedance of the orifice and a closed tube in parallel. For zero acoustic pressure at P we have

$$\frac{1}{Z_2} = \frac{1}{i\rho\omega/K} - \frac{1}{(\rho c/S_1) \cot(2\pi l_2/\lambda)}$$

from which we have

$$\lambda K/2\pi S_1 = \tan(2\pi l_2/\lambda) - \cot(2\pi l_1/\lambda) \quad \dots\dots(3a).$$

Closed tube as a side branch, figure 10(d). The side branch consists of an orifice at the junction of the tubes and the length l_3 of closed tube in series. The effective

impedance is that of the side branch and the stopped portion of the main tube in parallel.

$$\begin{aligned}\frac{I}{Z_2} &= \frac{I}{i\rho\omega/K - (i\rho c/S_3) \cot(2\pi l_3/\lambda)} - \frac{I}{(i\rho c/S_1) \cot(2\pi l_2/\lambda)} \\ &= -\frac{I}{(i\rho c/S_1) \tan(2\pi l_1/\lambda)}.\end{aligned}$$

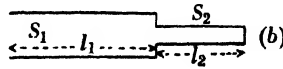
Therefore
$$\frac{2\pi S_1}{\lambda K} = \frac{S_1}{S_3} \cot(2\pi l_3/\lambda) - \frac{I}{\tan(2\pi l_2/\lambda) - \cot(2\pi l_1/\lambda)} \quad \dots\dots(4a).$$

Narrower tube of any length forming a constriction. Referring to figure 10 (e) and using the notation of the diagram, we write

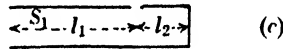
$$Z_q = i\rho\omega/K' - (i\rho c/S_1) \cot(2\pi l_2/\lambda) \quad \dots\dots(5a),$$



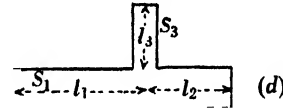
(a)



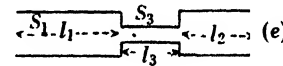
(b)



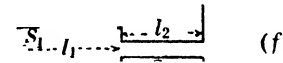
(c)



(d)



(e)



(f)

Figure 10.

where Z_q is the impedance facing the junction between tubes of areas S_3 and S_1 , and K' is the conductivity at the junction. This should be the same as the conductivity at the junction S_1 and S_3 but is here kept distinct to enable the equation to be verified.

$$\begin{aligned}Z_q &= \frac{i\rho\omega}{K} - \frac{iZ_q - (\rho c/S_3) \tan(2\pi l_3/\lambda)}{Z_q \tan(2\pi l_3/\lambda) S_3/\rho c + i} \\ &= - (i\rho c/S_1) \tan(2\pi l_1/\lambda) \quad \dots\dots(6a)\end{aligned}$$

for zero pressure at the pressure tube. Substituting for Z_q from (5a) and reducing we find

$$\begin{aligned}\frac{I}{K'} &= \frac{\lambda}{2\pi S_1} \cot(2\pi l_2/\lambda) \\ &+ \frac{(\lambda/2\pi S_3) \tan(2\pi l_3/\lambda) + (\lambda/2\pi S_1) \tan(2\pi l_1/\lambda) + 1/K}{(2\pi S_3/\lambda) \tan(2\pi l_3/\lambda) - 1 + (S_3/S_1) \tan(2\pi l_1/\lambda) \tan(2\pi l_3/\lambda)} \quad \dots\dots(7a).\end{aligned}$$

It will be seen that if l_3 is considered small and K identical with K' then equation (7a) reduces to

$$2\pi S_1/\lambda K = \cot(2\pi l_2/\lambda) - \tan(2\pi l_1/\lambda), \quad \dots\dots(8a).$$

which is the expression for an orifice in series with a stopped tube.

Length of open tube forming a termination. Referring to figure 10 (f), we write

$$Z_q = i\rho\omega/K'.$$

Hence, on substitution in equation (6a),

$$\begin{aligned} Z_2 &= \frac{i\rho\omega}{K} + \frac{\rho\omega/K' + (\rho c/S_2) \tan(2\pi l_2/\lambda)}{(i\rho\omega/K') (S_2/\rho c) \tan(2\pi l_2/\lambda) + i} \\ &= -(i\rho c/S_1) \tan(2\pi l_1/\lambda) \quad \dots\dots(9a). \end{aligned}$$

Which reduces to

$$\frac{1}{K'} = \frac{(\lambda/2\pi S_2) \tan(2\pi l_2/\lambda) + (\lambda/2\pi S_1) \tan(2\pi l_1/\lambda) + 1/K}{(S_2/S_1) \tan(2\pi l_1/\lambda) \tan(2\pi l_2/\lambda) - 1 + (2\pi S_2/\lambda K) \tan(2\pi l_2/\lambda)} \quad \dots\dots(10a).$$

As will be seen if l_2 is made very small K and K' become inseparable and the equation reduces to

$$\lambda K/2\pi S_1 = -\cot(2\pi l_1/\lambda),$$

which is the relation for a single orifice terminating a tube.

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DEMONSTRATION

A NEW DEMONSTRATION OF THE PHENOMENON OF BEATS *given 25 March 1938*
by D. A. RICHARDS, A.R.C.S., M.Sc., D.I.C., University College of Wales,
Aberystwyth

THE apparatus used in this demonstration is shown diagrammatically in figure 1. Two brass cylinders *A* and *B* of equal mass are supported by two identical vertical steel spiral springs *C* and *D*. *A* and *B* are connected by a light flexible string *E* which passes under a light pulley *F*, the diameter of which is equal to the horizontal

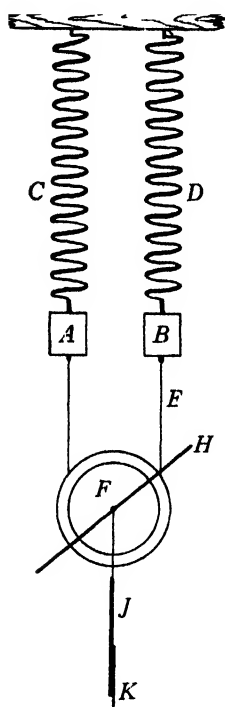


Figure 1.

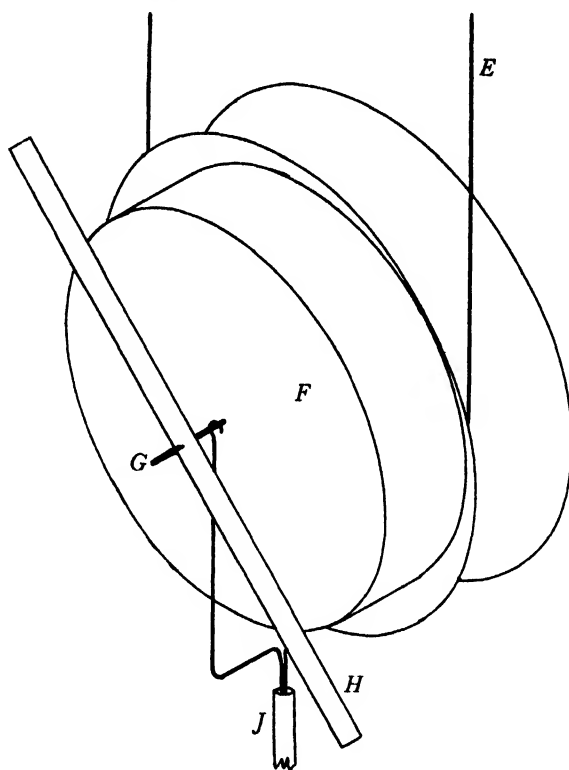


Figure 2.

separation of the axes of the springs. A large needle *G* through the centre of the pulley serves as an axle. Suspended from this is a light rod *J*, the attachment being effected with thin brass wire. To the lower end of *J* is fixed a vertical card *K* which serves as a damping vane to prevent oscillations of *J* in a vertical plane perpendicular to the axle and also to lower the centre of gravity of the system supported by the string *E*. Fixed to the axle *G* is a light pointer *H*. Details of these attachments can be seen in figure 2.

If *A* is at rest and *B* is set oscillating in a vertical line, *G* will oscillate in a

vertical line with half the displacement of B at any instant. Similarly B may be considered at rest and A displaced. If both A and B are displaced vertically the linear vertical displacement of G will be one-half the algebraic sum of the displacements of A and B . The difference in frequency between the two oscillating systems can be varied at will by the addition of a rider to the cylinder B . When this difference of frequency exists G will oscillate with a periodic change of amplitude.

Moreover, if A and B oscillate with the same amplitude, then when the oscillations are in phase, there will be no angular oscillation of the pointer H about G . Conversely when the two oscillations are out of phase there will be an angular oscillation of H about G . A difference of frequency between the two systems results in a continuous change in their phase difference. Hence the amplitude of the angular oscillation of H will vary periodically.

If the two springs are of equal strength, the two systems can be made to oscillate with the same amplitude by depressing J in a vertical line and then releasing.

Strictly speaking the two vibrating systems are not independent but are coupled, the degree of coupling being a function of the tension in the string E . The coupling can however be reduced to a small value by making the mass of the pulley small in comparison with that of A and B . The pulley was constructed by fitting a cardboard V groove to a large pill-box. H and J were light drinking straws. The mass of the system supported by the string is 13 g.

The apparatus is capable of giving good quantitative results. The individual vibrations were timed to an accuracy of about one part in 500, and the results are tabulated below. N_A and N_B are the frequencies of A and B respectively in cycles per second; N_F is the beat frequency.

N_A	N_B	$N_A - N_B$	N_F
1.072	0.862	0.210	0.2101
1.072	0.946	0.126	0.1266
1.072	1.010	0.062	0.0624

In the demonstration, a shadow of the apparatus was cast upon a white screen, the source of illumination being a bare arc. A considerable magnification could thus be obtained. The change in amplitude of the vertical oscillation of G can be more easily followed if the position of the centre of the shadow of the pulley on the screen is first marked when both A and B are at rest.

REVIEWS OF BOOKS

A Philosophy for a Modern Man, by Prof. H. LEVY. Pp. 287. (London: Victor Gollancz, Ltd., 1938.) 7s. 6d. net.

Prof. Levy evidently considers that the "modern man" for whom this philosophy is written is clever enough to study this difficult book, in which he not only expounds some of the fundamental concepts of physical science and mathematics but also attempts to apply these to socialism. The author, it will be remembered, is a professor of mathematics, a socialist, and a writer of works interpreting modern scientific conceptions for the non-specialist. It is not unnatural therefore that his methodical mind should encourage him to attempt to arrange this array of interests into some logical order—that is what he tries to do in this book. We have heard a good deal in recent years about the application of science to industry, but it is less usual to find science applied to the support of a political doctrine. Whether Prof. Levy is justified in the deductions which he draws from this application must be a matter for each reader to judge for himself and in any case this journal is hardly the place to discuss such matters. Some idea of the angle from which the book is written can perhaps be gleaned from the following quotation (p. 187): "It (the Darwinian theory) appears little more than the bald application of certain economic theories concerning the society of man, prevalent at the time of Darwin, to the animal world."

In the last chapters of the book will be found many of the well-known diatribes on socialism, which are not always in keeping with the more measured terms of the scientist adopted in the earlier part of the book. The author's conclusion appears to be that "the next age will be the classless society" and that no matter what else happens this stage is bound to come; therefore, he argues, we might just as well make deliberate plans to arrive at this stage by peaceful paths, rather than submit to world upheavals in trying to resist it.

The book contains some rather crude sketches and illustrations; and the print is small, making it a little trying to read.

For those scientists who interest themselves in political creeds and philosophies—and there are many who consider that it is the scientist's duty to do so—this book will be of considerable interest, whatever their own beliefs. The dust cover tells us that the book "may well have a profound effect on the thought of our generation". Perhaps it may.

H. R. L.

The Evolution of Physics, by A. EINSTEIN and L. INFELD. Pp. x + 320. (Cambridge: The University Press, 1938.) 8s. 6d. net.

Once again we have original workers of the highest rank attempting to explain physics to the layman. Unlike some of their predecessors, the authors do not stress the numerical or sensational aspects of recent work, and there is no description of the results of experiments on atom-splitting. Their task is harder, for they wish to make clear what is the nature of the change which has come over physics in the last 35 years, that is, since the advent of the relativity and quantum theories. To this end they trace in very brief outline the history, not of physics, but of physical thought, taking their origin with Galileo's realization of the law of inertia, without reference for example to Roger Bacon or any of the earlier thinkers on the matter.

The first change which they regard as significant was the introduction, or perhaps the stressing, of the concept of the "field" in place of particles and charges, and this step they

describe very clearly. It is a question for experiment to decide whether even the clearest description can bring out the significance to laymen, though there is no question that physicists who read the book will gain some insight which is not provided by a more detailed treatment, where the equations perhaps obscure the ideas. As we should expect, the philosophy of relativity is explained very clearly indeed. The last section deals with quantum theory (real quantum theory, not quantum additions to classical theory) and quite satisfactorily leads to an account of the difficulties which still confront us. In particular, there is the difficulty that nobody has yet succeeded in formulating the equations of quantum mechanics in a form invariant to the Lorentz transformation.

As far as externals go, the book is certainly made as easy as possible for the layman. There really is not an equation in it, even in disguise, and the illustrations show a delightful freshness. An author in search of flatland, in order to explain by analogy what a fourth dimension in space would be, has it ready to hand on the cinema screen, but Drs Einstein and Infeld are, I imagine, the first to realize this. They admit in their preface that they have given considerable thought to the properties of their ideal reader. They find that his great virtues are patience and perseverance, and they say that he is not to proceed to a fresh page till he has mastered the current one. Thus the book is not intended to while away an idle hour, but the greater effort required is compensated by the truer and clearer grasp of the subject which should result.

J. H. A.

Modern Physics, by G. E. M. JAUNCEY. Second Edition; pp. xviii + 602. (London: Chapman and Hall, 1937.) 22s. net.

It is never very difficult, and rarely quite fair, to criticize an elementary "Modern Physics" on the ground of its author's selection of material. Prof. Jauncey, for example, says nothing about the Zeeman effect, though he gives the theories of the reversible pendulum and the parallel-plate condenser, which are appreciably less "modern" in any sense of the term. Although the Zeeman effect has played a most important part in the development of electrical theories of matter and quantum theories of spectra, its omission here is clearly deliberate, as it had several pages in the first edition of 1933. On the whole, it must be said that Prof. Jauncey has made an excellent choice of topics—ranging from geophysics to nuclear physics—and has handled them in the manner of an experienced teacher and active physicist, without unduly stressing the portions which happen to be cognate with his own special subjects of research.

He starts from two very sound premises—viz., that some instruction in "modern" physics is desirable at a quite early stage in undergraduate courses, and that "it is necessary to know something of the history of physics in order to understand fully the meaning of modern physics". The book therefore begins with a short (34-page) historical introduction, and more attention than is usual in books of similar scope is given to both the historical and the numerical aspects of the topics under consideration. There are well-chosen numerical examples, with solutions, and the book is very suitable for use by first-year honours students of physics and other science students.

H. R. R.

A Text-Book on Crystal Physics, by W. A. WOOSTER, M.A., Ph.D. Pp. xxii + 295. (Cambridge: The University Press, 1938.) 15s. net.

No book devoted entirely to crystal physics has previously been published in English, and this in itself should be a sufficient excuse for the appearance of the present volume. The book is intended to be a textbook for students at universities and has been written with two objects—to present the classical treatment of the physical properties of crystals

in terms of tensor notation, and to indicate the lines of development of modern theoretical and experimental researches. With these objects in mind the mechanical, thermal, electrical, magnetic and optical properties of crystals are discussed and related where possible to the crystal structure or the nature of the constituent atoms or ions.

Certain subjects—ferromagnetic crystals, the mechanics of crystal lattices and much of crystal optics for example—are deliberately omitted, but a considerable amount of information is nevertheless packed into a relatively small space. One of the most desirable features of the book is, in fact, its conciseness and freedom from wasteful repetition, but as a result there is a tendency in places towards a certain amount of obscurity. Parts too will be difficult for the student who, with no previous knowledge of tensor notation, is equipped only with the knowledge of the “elements of physics, mathematics and crystallography” demanded of him.

The book as a whole, however, is one that will thoroughly repay study, and may be recommended to student and research worker alike.

J. T.

A Text-book of Physics, by L. B. SPINNEY. 5th edition. Pp. xii + 720. (The Macmillan Co.) 16s. net.

All who have recommended earlier editions of this textbook for junior students will welcome the new edition. Among other changes there is a new chapter on electron tubes and some brief reference is made to recent experimental work in nuclear physics. Much of the text has been revised and many new diagrams and problems have been added.

J. H. B.

Grimsehl's Lehrbuch der Physik, revised by R. TOMASCHEK. Vol. II, Pt. 2. Matter and Ether. Pp. viii + 456. (Leipzig: B. G. Teubner.) RM. 14.

The number of the editions of Grimsehl's textbook of physics (vol. I is in its ninth, vol. II in its eighth edition) speaks for the popularity of the work in Germany. This popularity can only be enhanced by the present volume. Prof. Tomaschek deals here with those properties of matter and radiation which directly involve atoms, electrons, protons, quanta, and the like. The treatment of this subject-matter is as comprehensive and up-to-date as could be required of a textbook. For example, the discussion of spectral lines embraces Landé's formula for the splitting factor g , Russell-Saunders coupling, superfine structure, the Raman effect and the isotope effect in band spectra. There is an excellent chapter on nuclear transformations (new in this edition) and short accounts are given of many special lines of work such as the scattering of X rays by liquids, Heitler and London's theory of the hydrogen molecule, ortho- and para-hydrogen, the inner photoelectric effect in crystals, the mode of origin of the northern lights, and axiality of light-emission. The more fundamental topics—the Rutherford-Bohr atom, the wave properties of the electron and so on—receive adequate treatment. A chapter on the electrodynamics of moving media finds a place, although it stands apart from the rest of the subject-matter.

The book is written in a clear, terse style. This is not unconnected with the fact that Prof. Tomaschek has been at pains to keep the experimental facts in the forefront. Where mathematical treatment is necessary the symbols are carefully defined, and space is devoted to the interpretation of the final result rather than to details of the proof. The text is embellished with 44 tables and 339 figures, included in the latter being a good selection of cloud-chamber photographs. There can be no doubt that this book reaches a very high standard, and the student who makes his acquaintance with the elements of atomic physics in its pages may count himself fortunate.

W. S. S.

The Flow of Homogeneous Fluids, by M. MUSKAT, Ph.D. Pp. xix + 763. (London: The McGraw-Hill Publishing Co. Ltd.) 45s. od.

The full title of this monograph, which is one of the International Series in Physics, is "The flow of homogeneous fluids through porous media". It is to be regretted that an abbreviated title should have been used on the cover, since it hardly conveys a precise indication of the scope of the volume.

The book deals in a thorough and comprehensive manner with the flow of liquid in porous media, a subject which is of considerable interest to the oil and gas industries. As the author points out, no attempt is made to solve what is really the fundamental physical problem in most actual cases of oil production, namely, the nature of the flow of gas-oil mixtures through porous media. This problem is one in the flow of heterogeneous fluids through porous media whilst the work is limited to the flow of homogeneous fluids. There is nevertheless a considerable number of problems of oil-production which can be solved by means of analytical results derived from a homogeneous-fluid theory, and there is a possibility that these problems will find still wider application in the future when more efficient use comes to be made of the possibilities of natural water drives.

This book has not been written simply as a college textbook. A thorough knowledge of the calculus and some familiarity with the elements of differential equations are assumed. The treatments of the problems have been given with such detail as to illustrate clearly the method of solution as well as the physical significance of the problem.

The treatment of the subject is divided into four parts. In the first the foundations are laid for the subsequent analytical treatment. The technique for determining the permeability of the medium is described. The empirical laws are formulated generally in three partial differential equations which form the starting-points for the analysis of the other three parts. The second part treats of problems of fluid flow in the steady state, the compressibility being formally neglected in the sense that the fundamental dependent variable satisfying Laplace's equation is taken as the pressure rather than the density. Potential-theory methods are then applied successively for the solution of two-dimensional and three-dimensional problems, gravity-flow systems, systems in which the porous medium is of non-uniform permeability, systems involving two homogeneous fluids, and finally multiple-well systems. In several cases experiments with sand and electrical models are described as means for obtaining results in cases in which the analysis becomes impracticable. Part 3 gives the treatment of typical cases of the non-steady-state flow of liquids, as based upon the Fourier heat-conduction equation with the fluid density as dependent variable. Part 4 in a single chapter gives the solutions for typical cases of gas flow, though here the analysis for the unsteady state is only approximate owing to the difficulty of obtaining exact solutions of the basic differential equation.

The methods employed are developments of potential theory and the theory of heat-conduction. A large part of the analysis is taken from papers and reports written by the author and his colleagues for the Gulf Research and Development Co. The volume impresses one with the vast amount of labour which has been expended on a highly specialized subject.

E. G.

An Introduction to Laboratory Technique, by A. J. ANSLEY. Pp. xiii + 313. (London: Macmillan and Co. Ltd.) 12s. 6d.

This book has been written primarily at the request of persons engaged in teaching physics, but it will also be of some use for laboratory assistants. It contains a résumé of several of the processes and certain of the techniques normally required in laboratories. The chapter headings are: Care of laboratory equipment; Cements, lutes and solvents; Electrical measuring and indicating instruments; Electric motors; Electro-plating; Glass-

blowing and glass-working; Graduation of apparatus; Insulators and their working; Mercury and its purification; Optical projection of lantern slides; Production of mirror surfaces; Soldering of metals; Storage cells; Miscellaneous; First aid treatment for laboratory workers; and Tables.

The author does not claim the book to be more than "an introduction" and it is written in a style which may be taken to assume that the reader has little or no previous knowledge of the subject. As the author himself points out, "no mere book-work, however, can completely fulfil the purpose for which this volume is designed; this can only be realised in its highest degree by patient and constant practice. Some of the recipes given are perhaps controversial; but on the other hand every experienced laboratory technician has his own favourite way of achieving an end which may be reached by several alternative methods." The occasional use of such unscientific expressions as "high degree of heat" or "in the best glasses the prolonged action of cold water merely attracts a minute trace of alkali," is unfortunate; and the continuous use of adjectives such as "carefully" "good" and "best-quality" detracts from the greater emphasis they would give if used more sparingly. The book contains some information which must be well known even to those for whom it is primarily intended. In table XX the units of specific heat are omitted and we are not told whether the coefficient of linear expansion is per °C. or per °F.

The book should be useful to those who find themselves without skilled laboratory assistants and have had no training in these matters. It is to be hoped, however, that in the near future the author will provide a similar book confined to useful practical hints and tips together with well-tried formulae and recipes for the benefit of those already familiar with the elementary parts of the subject; the reviewer believes there is a real demand for an up-to-date book of this nature.

H. R. L.

Photoelements and their Applications, by B. LANGE. Translated by A. ST JOHN. Pp. 297. (New York: Reinhold Publishing Corporation; London: Chapman and Hall, Ltd.) 27s. 6d. net.

The appearance of the first book exclusively devoted to the rectifier photoelectric cell, at times designated the barrier-layer, blocking-layer or Sperrschicht cell, and here the photoelement, heralds the rapid development of the latest addition to the growing family of photoelectric cells. Following the rediscovery of the rectifier photocell in 1928, fifty years after the original work of Uljanin, Adams and Day, Fritts and others, commercial development has proceeded at such a pace that new uses are constantly being found for these cells in illumination-measurements in industrial and research laboratories throughout the world. Unquestionably, then, a book, relieving one of the labour of referring to and appraising original papers, has become a pressing need.

The book under review is a somewhat free translation of one originally published in German in 1936. No effort has been made to include later work for the English version; hence in the main only work carried out up to the end of 1935 is detailed. A further limitation has been imposed by the surprising exclusion from the German version of any references (with few exceptions) to work carried on outside Germany. There is thus no mention of the many theoretical and experimental researches made in Russia, Holland, Belgium, France, the United States of America and Great Britain. In short, the scope of the book is limited mainly to researches made in Germany; and largely to the work of B. Lange. A detailed account in English of his work is, however, not without interest.

Considerable space is devoted to the cuprous-oxide cell. In later works, this cell will doubtless be of little more than historical significance, its place having already been taken by the more sensitive selenium rectifier photocell. There are, nevertheless, common features in the characteristics of the two types of cell. Many of the properties are, however, interpreted in terms of theories which have largely been superseded by the wave-mechanical

interpretation of the barrier-layer effect expounded by A. H. Wilson, Fowler, Frenkel and Joffé, Condon and others. Some of the difficulties have hence been resolved, though we have not as yet as complete an understanding of all the phenomena presented as could be desired.

The reader has to remain satisfied with a schematic diagram of the rectifier photocell reduced to its simplest terms without even a few details concerning the construction. Unpublished patent specifications are responsible for this omission. The general reader will consequently be much more interested in the very many ingenious applications fully described; this part of the book is to be commended. Here and there, Dr Lange permits his enthusiasm for his work to outweigh his usually sound judgement; an occasional tendency to belittle or minimize the errors possible in the use of these cells is apparent. The rectifier photocell always gives an answer innocently and with apparent assurance to the question "How much?" A timely warning on appropriate occasions concerning the lying-pensivities of these cells would have been useful.

G. P. B.

Mathematical Tables, Vol. VI; (Bessel Functions, Part 1). Prepared by the British Association Committee for the Preparation of Mathematical Tables. Pp. xx + 288. (Cambridge: The University Press, 1938.) 40s.

Here we have both an achievement and a memorial. It is now half a century since the British Association first appointed a committee to consider the preparation of mathematical tables, having in mind Bessel functions in particular. To it was appointed, among others, Prof. Alfred Lodge. The work went slowly at first, though various useful tables were included in the Annual Reports of the Association from time to time. With the War the work almost came to a standstill. Then the committee was reorganized, still numbering Lodge among its personnel, and in 1931 the first volume appeared, dealing in the main with trigonometrical functions. Four more volumes were published, and then at last the committee, having cleared the ground sufficiently, was ready to issue the first of the volumes dealing with Bessel functions. At a meeting of the committee of Section A last year the members were let into the secret that the new volume was to be dedicated to Prof. Lodge, though he was not to know it until he saw it in print. He died a few days before publication, but the inscription stands.

The volume is worthy of the work spent on it. It gives only the functions of the orders zero and unity, to eight decimal places, and covers directly the range up to $x = 25$, and indirectly up to 6000, whereas all previous sets of tables ceased before $x = 42$; and it goes without saying that the precautions taken against misprints are as thorough as can be devised, short of the use of photographic methods of reproduction from a script typed by a calculating machine.

J. H. A.

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SECONDARY-ELECTRON EMISSION FROM NICKEL COBALT AND IRON AS A FUNCTION OF TEMPERATURE

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AND

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A communication from the Research Staff of the M.O. Valve Company
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ABSTRACT. The evidence of other workers to the effect that the magnetic and structural changes which occur in ferromagnetic metals are accompanied by changes in the secondary-electron emission is critically discussed, and it is shown that this evidence is in many respects unsatisfactory. The authors have measured the secondary-emission coefficients for nickel, cobalt and iron at various primary voltages over a temperature range of about 400°C. , and find in all cases either no change or a slight and gradual fall in the coefficient with rising temperature, the latter effect probably being due to surface gas. No evidence was obtained of any discontinuous changes in secondary emission at the transformation points, though a change of less than 5 per cent could readily have been detected.

§ 1. INTRODUCTION

It has been shown in a number of experimental investigations* that the coefficient of secondary-electron emission from a metal surface is, in general, independent of the temperature of the emitter. Exceptions to this general rule have been reported in the case of ferromagnetic metals and metals which undergo a change of crystal structure at a certain temperature; for such metals it appears from certain published results that there may be abrupt changes in secondary emission at the temperatures corresponding to the magnetic or structural changes. Owing to the theoretical significance which may be attached to these findings, and also to the fact that the previous works on the subject are open to serious criticisms, it was felt that a further experimental investigation of this matter was desirable.

* For summary of these investigations see Kollath⁽⁷⁾.

§ 2. CRITICAL EXAMINATION OF PREVIOUS WORK

There have been two previous investigations dealing with the subject-matter of the present paper, the first due to Tartakowsky and Kudrjawzewa⁽¹⁾ and the second to Hayakawa⁽²⁾. Tartakowsky and Kudrjawzewa studied the secondary emission of nickel as a function of temperature, using primary voltages in the neighbourhood of 30. According to their data, an example of which is reproduced in the broken curve in figure 1, when the temperature of the metal is raised from 150 to 350° c. there is a continuous increase in the secondary emission. This is followed by an abrupt fall at the Curie point (358°), i.e. the temperature at which the metal loses its ferromagnetic properties, and a further and more rapid rise up to 445°. Substitution of copper for nickel, in a control experiment, resulted in a uniform linear increase of secondary emission with temperature being obtained, the rate of increase being about 12 per cent per 100° rise of temperature. The sudden fall in the amount of the secondary emission which occurred in passing through the

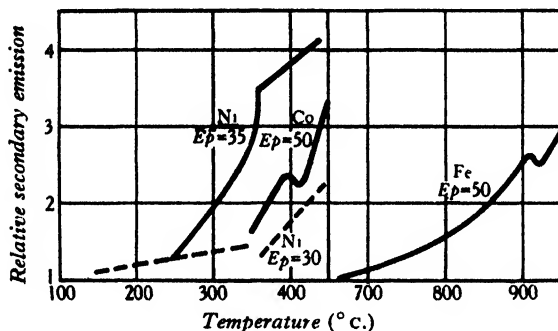


Figure 1. Variation of secondary emission with temperature. — Hayakawa; --- Tartakowsky and Kudrjawzewa.

Curie point of nickel was held to show that the conduction electrons of the metal, which Tartakowsky and Kudrjawzewa suppose to give rise to the major portion of the secondary emission, are also responsible for its ferromagnetic properties.

In considering the experimental method by which these results were obtained, it is clear that the authors were not able to collect and measure all the secondary electrons emitted by their target. They could not, therefore, measure the secondary-emission coefficient, i.e. the ratio of the number of secondary electrons emitted by the target to the number of primary electrons incident upon it. What they actually measured was the current due to a comparatively small fraction of the emitted secondaries which entered a Faraday cage placed at a distance from the target. Now the ratio of this measured current to the total secondary emission must have been determined by the orbits of the secondary electrons leaving the target, and the orbit of a particular electron will depend on its direction and velocity of emission, on the potential-distribution in the space outside the target, and also on the magnetic field, if any, in the space. It follows that the data of Tartakowsky and Kudrjawzewa cannot be directly related to the secondary-emission coefficient, or to any other quantity having a precise physical significance, unless the following conditions were

satisfied, over the temperature range employed: (1) constancy of angular distribution of the emitted secondaries; (2) constancy of energy distribution of the emitted secondaries; (3) constancy of potential of the glass walls; (4) absence of stray magnetic field due to the current in the filament used to heat the target.

It is not possible to say whether these conditions were satisfied, but the absence of any mention of their importance in the paper gives rise to some doubt as to the validity of the results obtained.

A further difficulty is presented by the large variation in the secondary emission from nickel over the temperature range on either side of the Curie point, and by the variation with temperature observed with copper, both of which effects were passed over without comment by the authors, though they would certainly not have been anticipated on the basis of earlier results.

Hayakawa^(a) studied the variation of secondary emission with temperature for nickel, iron, cobalt and certain nickel-iron alloys, using primary voltages from 20 to 125. He found in all cases a large variation of secondary emission with temperature. Typical examples of his results are reproduced in figure 1. For nickel and iron the slope of the curve relating secondary emission with temperature changed abruptly at the Curie point, whilst for iron and cobalt there was a kink in the curve at the temperature corresponding to a change in the crystal structure. Analogous results were obtained with the nickel-iron alloys. The data were interpreted by Hayakawa in the light of a theory developed by Richardson⁽³⁾, and quantitative evidence was adduced in support of the view that the secondary electrons were identical with Richardson's "structure electrons".

Whilst Hayakawa's experimental arrangement is not open to the objections which have been brought against the work previously discussed, his data nevertheless present such curious anomalies that they cannot readily be accepted. His results are not expressed in terms of the secondary-emission coefficient, even though it is stated that both the primary and secondary currents could be measured. Moreover, it is difficult to form a clear idea as to what quantity the term "secondary electron emission" as used by the author is intended to represent. Presumably it bears some relation to the secondary-emission coefficient, but it is not a relation of proportionality, as an examination of his figures will show. For example, the rates of variation of this quantity with temperature shown in his figures 8 and 9 differ by a factor of 2 from those given in his figure 10 for the same material under the same conditions. Even greater discrepancies are apparent when his figures 12 and 13 are compared with figure 14. Finally, it must be observed that the secondary emission from nickel at primary voltages of 19.5 and 22 apparently falls to zero at a certain temperature. It is also remarkable that Hayakawa found even larger variations of secondary emission with temperature, unassociated with any transformations, than Tartakowsky and Kudrjawzewa did, though like them he does not consider that point worthy of discussion.

For these reasons it was felt that Hayakawa's data could not be accepted as establishing beyond doubt the existence of a relationship between secondary emission and metallic structure.

§ 3. STUDY OF NICKEL AND COBALT

In the present investigation of the variation with temperature, if such variation occurs, of the secondary-emission coefficient for nickel and cobalt, a very simple experimental system shown diagrammatically in figure 2 was employed. A short tungsten filament F mounted axially in a cylindrical anode A served as the source of electrons, some of which, after passing through the tube G of length 10 mm. and internal bore 0.5 mm., fell on a target T of the material under investigation. This target, which was in the form of a tube of rectangular section, could be heated by passing a current through an insulated tungsten filament H , and its temperature could be measured by means of the thermocouple Th . The couple, which consisted of a pair of 0.1 mm. platinum and platinum-iridium alloy wires obtained from Messrs Johnson Matthey, was welded on to the target and sealed through the glass envelope of the apparatus. The tube G terminated in a circular nickel disc D , 10 mm. in diameter. The target, shown in plan in figure 2 (*b*), was electrically but not

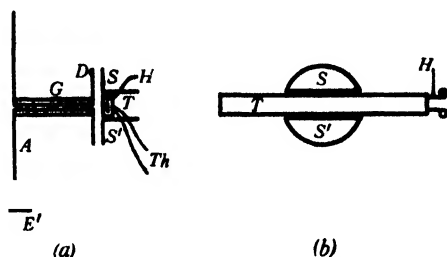


Figure 2. Electrode system used in the measurements.

thermally connected with segments SS' mounted on either side of its centre portion, the disc D and the target with its associated segments thus forming in effect a pair of parallel plates separated by a distance of 1.5 mm. The field in the neighbourhood of the centre of the target, when a potential-difference was applied between target and anode, was therefore approximately uniform and normal to the surface of the target. By this arrangement the necessity for the provision of a separate collecting-chamber was obviated, with the result that the target could be brought quite close to the electron gun G , and its dimensions, and therefore the energy required to heat it, could be kept small.

When the positive potential applied to the target was above that of the anode, only those secondary electrons emitted from the target with normal components of velocity sufficient to overcome the retarding potential difference were able to reach the anode, the remainder being returned to the target. In practice, therefore, a potential-difference of 150 v. between target and anode was sufficient to prevent the escape of all but a negligible fraction (probably less than 2 per cent) of the secondary electrons. This is illustrated by curve (*b*) in figure 3, which shows the variation of target current with target voltage, the anode voltage being fixed at 150 and the anode current maintained at 0.5 ma. by adjustment of the temperature of

the filament F . It will be seen that the target current was constant for retarding potentials in excess of 100 v., indicating complete suppression of the secondary current. This limiting value of the target current was taken to be equal to the primary current over the range of voltages in which the field between anode and target was in such a direction that all the secondaries emitted from the target were drawn over to the anode, the secondary current in this region being therefore the difference between this and the observed current. The ratio of secondary to primary current, i.e. the secondary emission coefficient, was thus readily obtained.

To check that the primary target current was independent of the target voltage over the whole of the voltage range employed in the measurements, a separate experiment was carried out in which the target was replaced by an elongated cylindrical collecting-chamber 3.0 mm. in diameter and 40 mm. long. With an

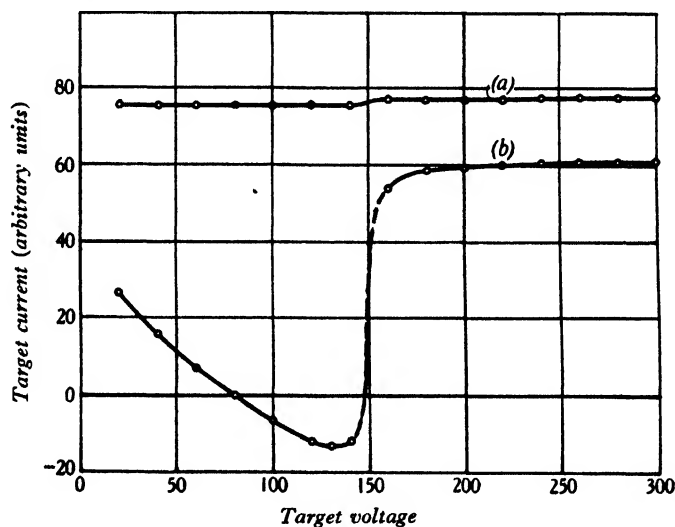


Figure 3. Variation of target current with target voltage.

anode voltage of 150, the current to this collector, for various collector voltages, was as shown in figure 3, curve (a). This shows that the target current was independent of the target voltage to within $1\frac{1}{2}$ per cent.

On account of the imperfect insulation resistance of the heater coating at the higher temperatures employed, it was found necessary to supply the heating current from an insulated battery, the target being then connected to one end of the heater. All the measurements were made with sealed-off tubes containing barium getter.

In the first investigation the target was of nickel. This metal undergoes a magnetic transformation at 358°C. but has the same crystal structure at all temperatures. After a preliminary degassing for 1 hr. at a temperature of 1100°C. , measurements of the secondary-emission coefficient were made as the temperature of the target was reduced from 525 to 110° . The results of these measurements, obtained with five different values of primary voltage, are shown in figure 4. There

appears to be a slight and gradual change of secondary-emission coefficient with temperature, due probably to changes in the amount of gas adsorbed on the surface of the metal. No evidence was obtained, however, of any sudden change in the secondary-emission coefficient at the Curie point.

That no disturbing effect was produced by the magnetic field due to the heating current was proved by the fact that switching off the current during the cooling of the target produced no change in the secondary emission.

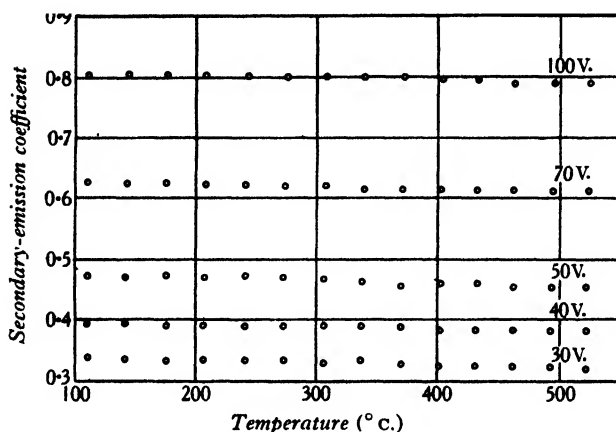


Figure 4. Secondary-emission coefficient for nickel as a function of temperature.

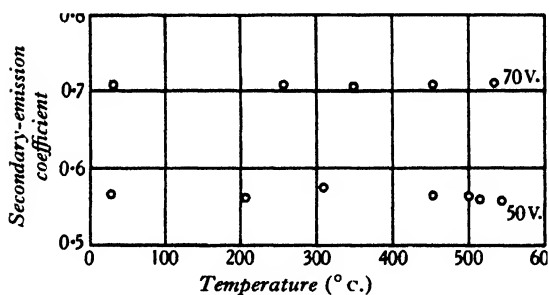


Figure 5. Secondary-emission coefficient for cobalt as a function of temperature.

The next metal studied was cobalt. The Curie point for cobalt is in the neighbourhood of 1150°C ., and a change from a hexagonal lattice, which is stable at room-temperature, to a face-centred cubic lattice has been reported by a number of observers to occur at a temperature between 400 and 500°C . The exact temperature at which the transformation takes place is not definitely established; it probably depends among other things upon the purity of the sample of cobalt studied and upon the rate of cooling. In a recent work Marick⁽⁴⁾ examined the structure of hot cobalt by X-ray diffraction and found the change to occur at about 490°C . during heating and at about 470° during cooling. The present experiments were concerned only with the structural change.

The cobalt was electrolytically deposited on to a nickel base to a thickness of about 0.05 mm. The target had been degassed before the assembly of the tube for 15 min. at 1000° C., and was subsequently heated to 1100° C. for a few minutes during the pumping. After the tube had been sealed off from the pump the latter treatment was repeated. Measurements of the secondary-emission coefficient were then made as the target-temperature was reduced in stages, 15 min. being allowed at each temperature for any possible time-lag in the occurrence of the transformation. As is shown in figure 5, there was no evidence of any appreciable change in the coefficient at any temperature from 20 to 540° C.

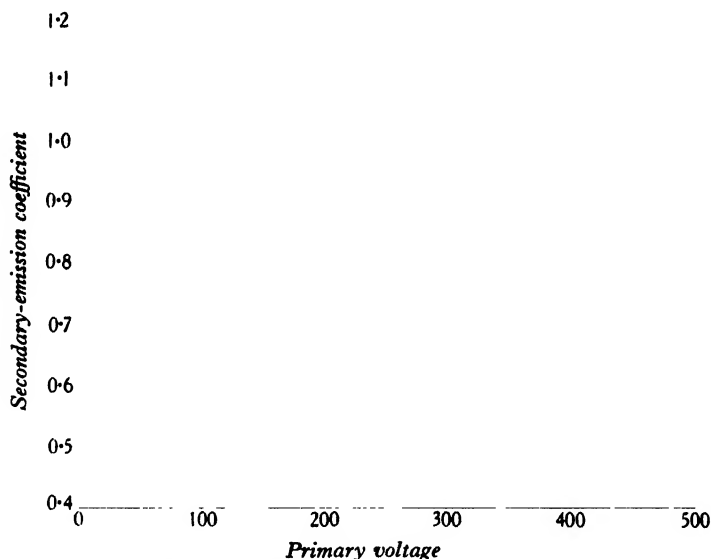


Figure 6. Secondary-emission coefficient for cobalt as a function of primary voltage.

Since there are few published data on the secondary-emission coefficient for cobalt, the curve of figure 6 is included in this paper. This gives the results of measurements of the coefficient, at room-temperature, for primary energies from 25 to 500 e.-v. Before taking these measurements the target was subjected to a further degassing at 1100° for 1 hr.

§ 4. STUDY OF IRON

In the study of iron the method of measuring secondary emission from filaments described in a previous paper by one of us⁽⁵⁾ was employed. This method was not used in the case of nickel and cobalt on account of the difficulty of accurately measuring very low filament-temperatures, but it was particularly suitable in the case of iron where a higher range of temperatures was required.

The target filament was of soft iron and had a length of 50 mm. and a diameter of 0.12 mm. The cathode was 12 mm. in length, and as it was run at the temperature required to give a total emission of 0.5 ma., its effective emitting portion, on account of the end cooling, was probably not more than a 5 mm. length at its

centre. The portion of the target filament subjected to electron bombardment was therefore also limited to a short length at its centre over which, under the conditions of operation, its temperature could be considered constant.

To avoid the possibility of contamination of the target by the evaporation of tungsten from the cathode, care was taken to avoid heating the cathode to a temperature higher than that necessary to give a space current of 0.5 ma. at any stage of the experiments. (The cathode filament had, however, been cleaned by flashing before the assembly of the tube.) Under these conditions a calculation showed that there was no possibility of contamination of the target occurring in this way.

In carrying out the measurements, the iron filament was heated to the required temperature by means of a current derived from an insulated battery. There was, of course, a potential-fall along the filament due to this current, but on account of the short length actually subjected to electron bombardment the potential-fall

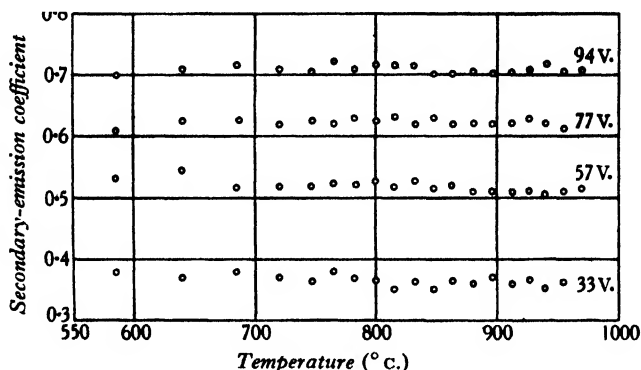


Figure 7. Secondary-emission coefficient for iron as a function of temperature.

along the effective length of the filament was never more than 0.2 v. The target was shunted by a high resistance, to the centre point of which the high-potential lead was connected; with this arrangement the primary voltage remained unaffected by changes in heating current through the target. A separate experiment was carried out to determine the temperature of the iron filament in terms of the heating-current through it. In this experiment an iron filament of the same length and diameter as that used in the secondary-emission measurements was mounted in a bulb together with an indirectly-heated iron cylinder in such a way that the centre of the filament could be matched for brightness against the cylinder in the background. The temperature of the cylinder was measured by an attached thermocouple, and the temperatures of the filament and of the cylinder were taken to be equal when the filament disappeared against its background.

The Curie point of iron is 770° C. and the transformation from a body-centred to a face-centred cubic lattice takes place at about 906° C. Both transformation points were included in the range of temperatures covered. In the carrying out of the experiment the target-temperature was first raised to 1000° C. for a few minutes for degassing purposes, and then maintained at 800° for 20 min. to ensure the

transformation to the body-centred structure. The temperature was then reduced to 585° and measurements were made as it was raised in steps to about 950° . The results of these measurements are depicted in figure 7. It is clear that there is no appreciable change in the secondary-emission coefficient either at the Curie point or at the temperature at which the structural change occurs.

§ 5. CONCLUSION

The accuracy of the foregoing measurements was such that a change of 5 per cent in the secondary-emission coefficient either at the Curie point (for nickel and iron) or at the temperature of the crystalline transformation (for cobalt and iron) would have been apparent. From the fact that no such changes were detected it must be concluded that such transformations have no significant influence on the secondary-emission phenomenon.

These findings are in contrast with those of Tartakowsky and Kudrjawzewa and of Hayakawa referred to earlier in the paper. Reasons have, however, been given for doubting the evidence upon which those authors sought to prove the existence of discontinuous effects at the transformation points.

A further paper, published by Davis⁽⁶⁾, has some bearing on the subject of the present investigation. Davis, in a study of the secondary-emission coefficient of cobalt as a function of the primary voltage, was able to obtain a stable and reproducible curve after prolonged heating at a yellow heat. If, after this condition had been achieved, the target was raised for a few minutes to a temperature near the melting point of cobalt (during which rapid evaporation of the metal occurred), an entirely different curve was obtained. Further heating at the previous temperature failed to cause a reversion to the preceding type of curve. The measurements were made with the target cold in all cases.

In attempting to explain this peculiar behaviour, Davis suggested that the appearance of the second form of curve might have been associated with a change from the face-centred to the hexagonal structure when the temperature was raised above 1150° C., a change for which there was a certain amount of evidence from other sources. Now, firstly, if there were such a reversion to the hexagonal structure above 1150° , it would be surprising if it were not reversible; that is to say, on the lowering of the temperature again into the 490 – 1150° region the metal would be expected to return to the face-centred cubic structure. Secondly, the evidence of Marick⁽⁴⁾, who worked up to a temperature of 1187° C., suggests strongly that the reported change of structure at 1150° does not in fact exist.

A different explanation must therefore be sought for the phenomenon observed by Davis. It seems not unlikely that the diminution of secondary emission which he found after the high-temperature treatment may have been the result of etching of the surface produced by evaporation of the metal, for it is known that the effect of roughening the surface of a metal is to reduce its secondary emission.

§ 6. ACKNOWLEDGEMENT

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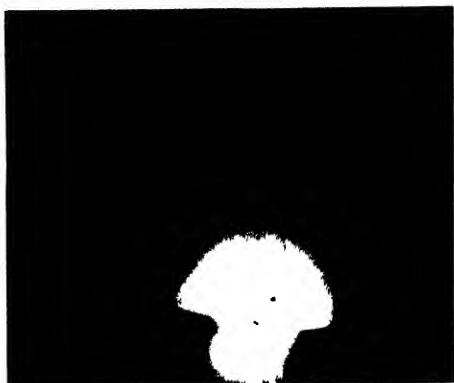


Figure 1.

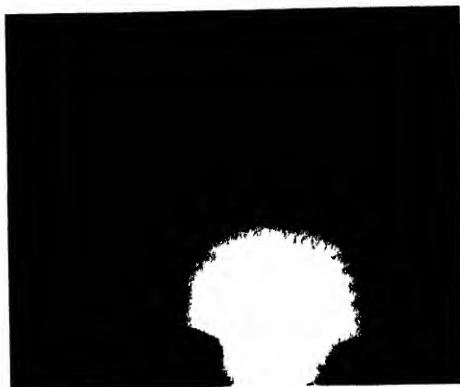


Figure 2.



Figure 3

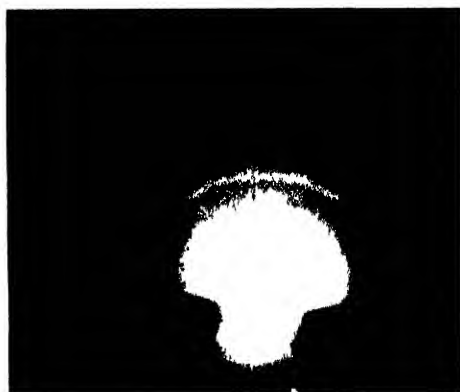


Figure 4.



Figure 5.



Figure 6.

DIFFRACTION OF ELECTRONS BY OXIDE-COATED CATHODES

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ABSTRACT. Electron-diffraction methods have been used to examine the surfaces of thermionic oxide-coated cathodes. The nickel cathodes were coated with a paste containing a solid solution of barium and strontium carbonates, and the diffraction camera was fitted up with ovens so that getter pellets could be fired off at suitable stages during the activation. These cathodes, after activation by heat treatment to give good emission, gave patterns of strontium oxide alone when no getter had been fired off, but gave patterns of magnesium oxide along with strontium oxide when the getter pellet (barium-magnesium alloy) had been fired off during the activation. Cathodes consisting of barium carbonate alone before activation gave patterns of barium oxide after activation, whereas cathodes consisting of strontium carbonate gave patterns of strontium oxide after activation.

§ 1. INTRODUCTION

IN an earlier paper by Gaertner⁽¹⁾ it was pointed out that if oxide cathode surfaces are examined by means of X rays the depth of penetration of the rays is so great that the photographs do not give information about the active surface layers, but give the general composition of the cathode coating.

An X-ray examination has been carried out by Benjamin and Rooksby⁽²⁾. The cathodes were activated in a high vacuum and the X rays were passed on to the cathode through thin-walled glass tubes. Thus the X-ray diffraction patterns were obtained without exposing the cathodes to air. Benjamin and Rooksby found that the activated layers consisted of mixed crystals of strontium oxide and barium oxide and that the proportion of barium oxide diminished if the cathodes were overheated, the emission having a maximum value corresponding to a cathode composition of approximately 60 per cent of strontium oxide and 40 per cent of barium oxide. They did not hope to find evidence on the presumably monatomic layer of alkali-earth metal on the cathode surface, which has often been considered to be responsible for the high emission that can be obtained from suitably activated cathodes.

Gaertner then repeated the experiments using electrons instead of X rays, and the detection of such a thin surface layer of barium became much more probable. Gaertner did not find any evidence for the existence of the barium layer; moreover his results differed from those obtained by Benjamin and Rooksby in that he obtained good patterns of strontium oxide by reflection from the cathode surface and little or no definite evidence of barium oxide.

It is known that barium oxide leaves the cathode by evaporation more readily than strontium oxide, and Gaertner came to the conclusion that the outer surface of a normally activated cathode loses its barium oxide component almost immediately, and strontium oxide remains predominant. Gaertner also obtained some hexagonal and tetragonal patterns. The hexagonal patterns, which appeared when the vacuum had not been good, remained unexplained. The tetragonal patterns were attributed to hydroxides of barium and strontium, and were found when the emission had been lost as a result of presence of water vapour.

The present work is a repetition of Gaertner's, under rather better vacuum conditions. It has been carried out in the hope of detecting the layer of barium on the surface and also to see if Gaertner's evidence for the apparent absence of barium oxide could be corroborated. The effect of getter-firing also has been investigated, and the contamination of the cathode-emitting surface due to it has been examined. The active surface of homogeneous single emitters, such as strontium oxide and barium oxide alone, has also been examined by electron-diffraction methods.

§ 2. APPARATUS

The electron-diffraction camera was of the Finch⁽³⁾ type, and for most of the work a gas discharge tube, fed from a hydrogen supply through an adjustable leak, was used as the source of electrons. A thermionic hot-wire cathode was used also. This is more difficult to control and gave the same results as the gas discharge in hydrogen.

At first a good many attempts were made to obtain patterns from standard valve cathodes such as those used for the output pentode. This cathode is 3 mm. wide and 40 mm. long and was mounted so that the beam passed across the surface of the cathode in a direction parallel to the 3.0 mm. edge. However, no patterns of any value at all could be obtained in either the fresh or the activated state. These cathodes had been coated with the mixed barium and strontium carbonates by means of the aerograph spray gun, as used for valve-production. The next step was to increase the width of the cathode so that more of the cathode surface would present itself to the electron beam. The cathodes were made progressively wider until, when they were approximately 1 cm. wide, some type of pattern began to appear. The patterns were still very poor, however, until the spray method of coating was abandoned. It was found that much better photographs could be obtained if the carbonate suspension was allowed to drop on to the cathode from the tip of a glass rod. The cathode was then tilted up and down, so that the mixture could run all over the surface, and then the cathode was put away with the surface arranged in a perfectly horizontal plane, so that the mixture could dry to a uniform depth over its surface. If too much suspension was placed on the cathode, it took longer to dry, the surface was fairly rough, and poor photographs were obtained. Microscopic examination indicated that spraying, under various conditions, always gave a much rougher surface than the flow method. Rather thicker carbonate mixtures had to be used when the flow method was adopted.

The cathode, in its final form, consisted of a built-up nickel block, the active face being sheet nickel 0.5 mm. thick. The back face was made up of nickel sheet 0.150 mm. thick. These sheets both measured 10 mm. by 30 mm., and they were welded to the support wires of an ordinary valve stem, one sheet on each side. The space between the nickel sheets was filled up with ceramic insulators of the kind used in certain types of indirectly heated valve cathodes. Tungsten wires were threaded through the ceramics and connected up in series. The normal rating for such a cathode inside the diffraction camera at a temperature of approximately 800° C. would be 35 v., 1.5 amp.

The anode was a sheet of nickel, a little larger in area than the cathode, and was mounted on the same stem as the cathode and situated approximately 7 mm. from the active surface. The cathode lead and one of the heater leads were joined together and earthed to the diffraction camera. The other heater lead and the anode leads were brought out of the apparatus through insulated tubes of glass sealed with white wax of high melting point.

Another side flange on the apparatus carried a glass tube through which two pairs of thick-gauge wires were taken. These were attached, inside the camera, to two tungsten spirals which carried small quartz ovens. The tungsten wire was strong enough to hold the small quartz tube without any additional support. Two Kemet (barium-magnesium) getter pellets of standard type were placed in these ovens just before the apparatus was evacuated at the beginning of an experiment, and the getters could be fired off as desired during the processing and activation of the cathode.

§ 3. RESULTS

The carbonate mixture. The photographs of the unactivated cathodes were never very good, and different degrees of ball-milling made very little difference. The measurements of the principal lines were, however, quite consistent, and these are given in table 1. A photograph of the unactivated cathode is reproduced in figure 1.

Table 1. Unactivated carbonates; values of d/n (Å.)

<i>m</i>	2.09
<i>m</i>	1.85
<i>w</i>	1.61
<i>w</i>	1.44
<i>m</i>	1.29
<i>w</i>	1.18
<i>w</i>	1.04
<i>w</i>	0.95

The material used was actually a solid solution of barium and strontium carbonates—containing approximately 57 per cent of barium carbonate and 43 per cent of strontium carbonate, and a calculation of the spacing of these carbonates gives so many values of d/n near to those in table 1 that it is useless to attempt to accord indices to the reflections observed. A further examination of cathodes coated initially with a mechanical mixture of approximately equal parts of barium carbonate and strontium carbonate is in progress.

The activated cathode. The cathode was then heated at a temperature of 1000° c. for four minutes. In some cases the activation was carried out by heat treatment only; in other cases additional activation was given after the heat treatment by drawing a current from the cathode at 800° c. for ten minutes. After activation the cathode was allowed to cool down to approximately 50° c. and a photograph was taken. The ring pattern was usually visible on the fluorescent screen, and so the cathode could be set at the best angle for reflection.

In many cases, when no getter had been fired off in the tube, the patterns were due to strontium oxide, but slight traces of other components could sometimes be seen. The measurements from such a pattern are given in table 2, along with the calculated values for strontium oxide in column 2. Column 3 gives the spacings found by Gaertner in the paper already referred to. A photograph of an activated layer is reproduced in figure 2.

Table 2. Activated cathode with no getter-firing; values of d/n (A.)

Activated cathode	Strontium oxide (calculated)	Gaertner
2.935	2.973	2.95
2.535	2.575	2.545
1.810	1.821	1.82
1.545	1.522	1.545
1.483	1.487	1.48
1.272	1.287	1.28
1.169	1.15	1.15
1.054	1.052	1.04
0.990	0.991	—
0.910	0.910	0.904
0.865	0.871	0.855

The patterns of strontium oxide, for which measurements are given in table 2, were obtained without firing any getter, and emission was quite good. The spacings agree so closely with those of strontium oxide that there is no evidence for a solid solution of the mixed oxides of strontium and barium. In some cases a number of extra lines appear and the patterns are so complex that a direct interpretation is not possible. In the later experiments, where getters were fired before and after activation, some excellent and well-defined patterns were obtained. A typical pattern of this type is reproduced in figure 3. Measurements from this pattern are given in table 3, and the values of d/n for barium, strontium, barium oxide are also given in columns 3, 4 and 5 respectively. It is evident that the pattern cannot be attributed to any of these substances. This type of pattern was obtained only when the Kemet getter (barium-magnesium alloy) had been fired within the tube. This pattern can be easily identified as that of magnesium oxide, and is found when the barium-magnesium getter cleans up the vacuum. A reflection photograph of magnesium oxide is reproduced in figure 4.

The cathode emission does not appear to drop in the least in consequence of this layer of magnesium oxide. A cathode was then sealed up on a standard valve pinch and activated on a bench pump. After activation the getter was fired and then the

assembly was sealed off; it was later broken open and fixed in the diffraction camera for examination. A good pattern of magnesium oxide was again obtained, resembling in all respects that given by the cathodes which had been activated in the diffraction apparatus. It seems that the normal cathodes will also have a surface layer of magnesium oxide, as received from valve production, and so it was considered desirable to examine the emission from cathodes (Ferranti type D 4) specially coated with magnesium oxide in various ways. From a layer of magnesium oxide sprayed over the standard emitting surface (1 mg. per cm²), the total emission under specified conditions was 60 ma.; with magnesium oxide alone on cathode, it was 0.25 ma.; with magnesium oxide mixed in equal parts with the standard cathode spray it was 40 ma.; with the standard spray without any contamination by magnesium oxide it was 240 ma. These results indicate that any appreciably thick layer of magnesium oxide can seriously lower the cathode emission.

Table 3. Activated cathode with getter firing; value of d/n (A.)

Activated cathode after getter firing	Magnesium oxide	Barium	Strontium	Barium oxide
2.465	2.430	3.540	3.508	3.193
2.090	2.100	2.506	3.038	2.765
1.485	1.485	2.048	2.148	1.955
—	—	1.774	1.832	1.667
1.200	1.215	1.586	1.754	1.596
1.046	1.050	1.449	1.519	1.382
—	—	1.341	1.394	1.269
0.935	0.938	1.254	1.358	1.237
0.845	0.856	1.183	1.240	1.129
—	—	1.120	1.169	1.064
—	—	1.069	1.074	0.977
—	—	1.023	1.027	0.935

There is no doubt that on the normal valve assembly the cathode is not exposed to the direct path of the getter particles, and so the deposition of magnesium oxide would not be very great. There is every chance, however, that the cathode may receive some slight contamination from magnesium oxide, especially if the valve is very gassy before the getter is fired off. It must be remembered that in our experiment with the bench-pumped cathodes the bulb had to be broken open just before use, and if there was a deposit of metallic magnesium it would certainly oxidize to give magnesium oxide. The experiments do indicate, however, that the getter gives contamination, and our experiments in the diffraction chamber, where the contamination is certainly magnesium oxide, make it appear that it would also be magnesium oxide originally in the bench-pump evacuation. The bench-pump vacuum before getter-firing would not be as good as that in the diffraction chamber.

When this magnesium-oxide layer has appeared it cannot be removed by the most elaborate flashing schedules. The magnesium-oxide patterns are merely improved by reheating, and if the specimen is exposed to air after cooling down again the pattern is still magnesium oxide, even before any reheating. The pattern is

definitely weaker and rather more diffuse after an exposure to atmospheric conditions, but it returns to its original type when reactivation is carried out.

On one occasion a different pattern was observed after getter-firing. This was carried out with the cathode coated with carbonates, but not heated at all. The surface remained unaltered after several exposures to air and gave a very sharply defined pattern of rings, figure 5. The cathode was of a rather dull metallic grey appearance, as opposed to the white surface previously observed. The material could not be barium or magnesium because of its stability in air, and was proved not to be magnesium oxide or barium oxide by measurement of d/n . So far, these rings are not understood. After the cathode had been heated up in vacuo and activated the pattern disappeared and became that of magnesium oxide. This took place without any additional getter-firing, and the material itself must have contained magnesium in some form.

Strontium carbonate alone. When the cathodes were coated with strontium carbonate alone, the patterns originally were poor, just as in the case of the mixture of barium and strontium carbonates. After activation the pattern of strontium oxide was plainly visible, provided no getter was fired, figure 6. If the getter was fired the pattern was that of the usual magnesium oxide + strontium oxide. If the cathodes were shielded from the getter beam the patterns were sometimes of strontium oxide and sometimes of strontium oxide + magnesium oxide. The emission from pure strontium-carbonate cathodes was, of course, very low. The following figures were taken from actual valve assemblies, to show the relative difference in the emission values of strontium oxide and barium oxide.

Table 4. Relative emission (ma.) under standard conditions

Barium carbonate	50
Strontium carbonate	9
Suitable mixture	170

Barium carbonate alone. Cathodes were coated with a barium-carbonate mixture and the patterns just after coating were very poor. After activation the patterns were not nearly as good as those from strontium carbonate, but in some cases they were good enough to allow the material to be identified as barium oxide. The emission from these cathodes was much better than that from the strontium-carbonate cathodes, in accordance with the figures given in table 4.

During experiments with very thin cathode coatings, it was suspected that nickel-oxide lines made their appearance during activation. This was later found not to occur, but while the matter was being investigated a rather interesting experiment was carried out on standard valve-production schedules. The cathodes of some output pentode valves of the Ferranti type PT 4D were oxidized to a pale blue colour by heating in air prior to their being sprayed with the mixed carbonates. These valves were assembled and were then given the normal production schedule for their type. After standard ageing, they showed about three times the normal softness current. They were re-aged and a little more getter was fired off; then they were within the recognized limits of hardness and the emission was quite up to the normal standard. These experiments with nickel oxide are hardly parallel to those

carried out with magnesium oxide earlier, but they indicate that appreciable oxidation of the nickel base is not a serious matter.

The nickel-oxide rings were normal and did not give the extra reflections sometimes reported. This was true even if the oxidation was carried out in the highest vacuum obtainable consistently with oxidation of the surface.

§4. SUMMARY AND CONCLUSIONS

Gaertner reported some special patterns of hexagonal type when the cathode was partially poisoned by activation in a poor vacuum. He also reported a tetragonal structure when the cathode had been activated in a trace of moisture and completely poisoned. In some cases patterns were obtained in the present research which could not be explained in terms of known structures, but patterns corresponding to Gaertner's hexagonal and tetragonal types were not seen.

In general, however, Gaertner's conclusion that the activated oxide cathode presents a surface layer of strontium oxide has been verified. Gaertner's unactivated carbonate coating consisted of a mechanical mixture of the barium and strontium carbonates, whereas in the present research the carbonate was a solid solution of barium and strontium carbonates. In both cases, therefore, it appears that the final activated cathode has a surface layer of strontium oxide which presumably rests upon a solid solution of barium and strontium oxides, as was found by X-ray examination by Benjamin and Rooksby⁽²⁾.

As regards the monatomic layer of barium postulated by Becker and Sears⁽⁴⁾, we must remember that even if this layer were present it would not give an ordinary barium pattern. It would give either a typical two-dimensional grating pattern or a diffuse liquid pattern, according as the arrangement of barium atoms was regular or random. Now the lattice constant of strontium oxide is 5.150 Å. and that of barium is 5.015 Å., and so it is possible that the barium could be attached to the strontium-oxide lattice by linkage to the oxygen atoms of the strontium-oxide structure. If this were the case the adsorbed barium atoms would be virtually part of the strontium-oxide lattice and merely modify very slightly the intensity of the reflections from the strontium-oxide spacings, and its presence would be very difficult to detect even by electron-diffraction methods. If it were adsorbed in this way it would presumably be ionized and have a larger interatomic distance than would be natural for its ionic state, and the resultant surface field could perhaps give rise to the low work function and consequent high thermal emissivity of oxide-coated cathodes.

§5. ACKNOWLEDGEMENTS

In conclusion, I should like to thank Ferranti Ltd. for providing facilities for this research and for permission to publish the results. In particular my thanks are due to Mr A. L. Chilcot for many helpful suggestions and discussions.

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THE FLASHING CHARACTER OF AERODROME FLOODLIGHT BEACONS

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AND

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ABSTRACT. A simple mathematical method is developed for calculating the frequency of the flash, and the distribution of intensity during the flash, when a floodlight is tilted and rotated so as to form a flashing beacon. The results of a number of typical calculations are given as diagrams and these may be used to estimate the results given by other distributions and conditions which would not be so readily calculated. Comparison is drawn between the various methods of tilting and the ideal requirements of an airway beacon.

§1. INTRODUCTION

AN aerodrome floodlight consists of an optical system so arranged as to emit light in a beam of narrow vertical divergence and wide horizontal divergence. Its purpose is, as its name implies, to illuminate the surface of an aerodrome to facilitate night landings.

An aerodrome beacon is intended to draw the attention of a distant pilot and to inform him of the name and position of the aerodrome which he is approaching. It has a flashing character which may be a distinctive Morse letter or may be only a regular flash similar to that of many marine lighthouses. It differs from a lighthouse in that it must give its indications in three dimensions, and it may consist either of a network of discharge tubes or of an optical system rotating about a vertical axis and projecting a beam whose intensity is high in the horizontal direction, with diminishing intensity up to about 20° above the horizontal. In the latter case, the intensity is usually so distributed that a pilot approaching the beacon at some given height and in some given state of the weather will receive substantially constant illumination after he has come within range of the beacon.

For reasons of economy, it is sometimes desired to make one apparatus serve for both purposes. The optical requirements for a floodlight are much more stringent than those for a beacon, and so the problem becomes that of finding the most efficient way of employing a typical floodlight apparatus as an aerodrome beacon. This paper is not concerned with either the type of floodlight or the mechanical details of mounting, but deals solely with the optical and geometrical aspects of the problem.

The obvious way of converting the floodlight to a beacon is to tilt it so that the beam becomes an elevated sheet, and then to rotate it about a vertical axis so that the whole azimuth is swept by the beam during one revolution and a flashing character is imparted. Three systems of tilting have been used in this country, but hitherto no details of the type of flash resulting from each have been computed. The three methods are: (I) tilting about an axis normal to the direction of maximum intensity—the general practice until 1932; (II) tilting about the direction of maximum intensity (British patent 426,222); (III) tilting about an axis inclined to the direction of maximum intensity (British patent 452,933).

This paper discusses the effects of these three methods and their compliance with the relevant requirements for a beacon, which are (a) that the beam-intensity should be a maximum along the horizontal, falling progressively as the elevation of the observer increases, with little or no light above 20° from the horizontal and (b) that the character of the flash—i.e. its duration and periodicity—should be independent of altitude. There are, of course, other requirements for a beacon, but these are not fundamental to an investigation of flash characteristics.

§ 2. THE GENERAL CASE OF A TILTING BEAM OF WIDE HORIZONTAL AND NARROW VERTICAL DIVERGENCE

Consider a very thin sheet of light emitted by an aerodrome floodlight at an angle β above the horizontal. This light lies on the surface of a cone whose semi-angle is $\pi/2 - \beta$, whose axis is vertical and whose equation is:

$$z = \tan \beta \cdot \sqrt{(x^2 + y^2)} \quad \dots\dots(1).$$

Similarly, for light emitted at a divergence of $-\beta$, there will be a conical surface below the horizontal, which is given by the negative values of z in equation (1).

If the double cone be now tilted so that its axis is at an angle δ to the vertical OZ and lies in the XZ plane, the equation to the surfaces becomes

$$(z - x \tan \delta)^2 - y^2 \tan^2 \beta \sec^2 \delta = (x \tan \delta - x)^2 \tan^2 \beta \quad \dots\dots(2).$$

Reference should be made to figure 1, which illustrates the angles involved. This equation may be used either to define the limits of a beam, where β corresponds to the maximum divergence, or may be used to calculate the position of an elementary sheet of light at an angle β within the beam.

A pilot poised at an angle γ above the horizontal receives the same intersection of a rotating beam as he would see by flying in a circle round a vertical axis through the beacon while it is stationary. His course would be given by

$$\left. \begin{aligned} x &= \sin \theta \\ y &= \cos \theta \\ z &= \tan \gamma \end{aligned} \right\} \quad \dots\dots(3),$$

where the radius of his course is unity and θ is his horizontal angular position with reference to the Y axis.

Substituting (3) in (2) and solving for θ , we have

$$\sin \theta = \tan \gamma \cot \delta - \sec \gamma \sin \beta \operatorname{cosec} \delta \quad \dots\dots(4).$$

Alternatively, solving for β , we have

$$\sin \beta = \cos \gamma \cos \delta (\tan \gamma - \sin \theta \tan \delta) \quad \dots\dots(4a).$$

Equation (4) gives two solutions for θ and $(\pi - \theta)$ corresponding to the four values of the angle in the horizontal plane which are the projections of the pilot's position when he enters and leaves the tilted beam. These solutions apply to the three types of floodlight beacon, since no restrictions have as yet been applied to the distribution of intensity.

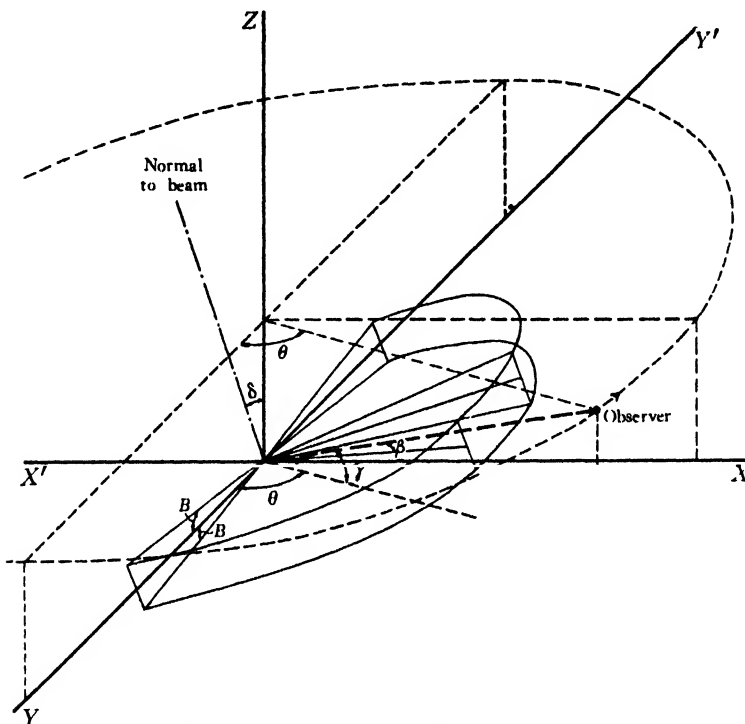


Figure 1. Isometric drawing of tilted beam.

§ 3. THE DISTRIBUTION OF LIGHT IN THE BEAM

The horizontal polar distribution of intensity (candle power) of certain types of floodlight may be represented sufficiently closely by the relation

$$I' = I_0 \cos \phi \quad -\pi/2 < \phi < \pi/2 \quad \dots\dots(5),$$

where I' is the horizontal intensity at an angle ϕ away from the maximum intensity I_0 . Various floodlights will have other distribution curves, but it has been found that all types which are suitable for tilting as beacons have distribution curves which lie between those represented by equation (5) and the following equation

$$I' = I_0 \cos^2 \phi \quad -\pi/2 < \phi < \pi/2 \quad \dots\dots(5a).$$

The two equations are shown graphically in figures 2a and 3. It will be seen later that the difference between these two limiting curves has only a small effect on the distribution in the tilted beam, and no effect on the flashing character of the beam.

The polar distribution in the vertical section of the beam at any value of ϕ is represented closely by the relations

$$I = I' \cos^2 (\pi\beta/2B) \quad -B < \beta < B \quad \dots\dots(6),$$

where I is the intensity at (ϕ, β) and B is the vertical semidivergence of the beam at ϕ . This is shown in figure 2 b. For purposes of calculation it is permissible to

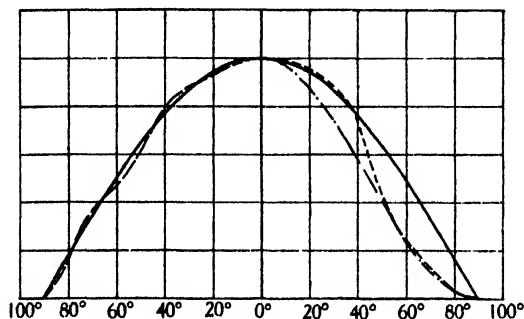


Figure 2 a.

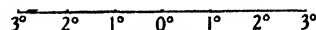


Figure 2 b.

Figure 2 a. Horizontal distribution of intensity. — $\cos \phi$, equation (5); - - - $\cos^2 \phi$, equation (5 a); — — — 10 kw. lens floodlight; - - - - 9 kw. G.E.C. mirror floodlight.

Figure 2 b. Vertical distribution of intensity. — — $\cos^2 (\pi\beta/2B)$, equation (6); - - - - 10 kw. lens floodlight.

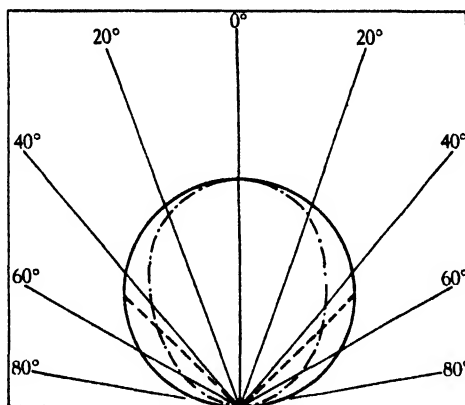


Figure 3. Horizontal polar distribution of intensity. — cosine, equation (5); - - - restricted cosine; - · - \cos^2 , equation (5 a).

assume that B is independent of ϕ . The whole polar distribution of intensity from this floodlight is then given by the relation

$$I = I_0 \cos \phi \cos^2 (\pi\beta/2B) \quad -\pi/2 < \phi < \pi/2, \quad -B < \beta < B \quad \dots\dots(7).$$

Using equation (5 a) instead of equation (5), we may write the polar distribution of the \cos^2 type as follows

$$I = I_0 \cos^2 \phi \cos^2 (\pi\beta/2B) \quad -\pi/2 < \phi < \pi/2, \quad -B < \beta < B \quad \dots\dots(7 a).$$

The restricted-cosine distribution is given by equation (7) with limits

$$-\pi/4 < \phi < \pi/4.$$

§ 4. APPLICATION OF THE THREE METHODS OF TILTING

In § 2 the general case of the tilting of a beam occupying 360° in azimuth has been considered. Equation (5) shows how the light from an actual floodlight only extends over 180° in azimuth and how the intensity in this region varies. The tilting represented by equation (2) applies to elevation of the beam about OY as axis, so that the beam is raised above OX and depressed into the ground in the OX' direction. It only remains to draw the polar curve on the tilted surfaces, with the peak intensity in the appropriate direction relative to OY , the axis of tilting, and the same equations will represent three methods of tilting described in § 1.

Let the peak intensity of the beam be at an angle α to OY , measured in the median plane of the beam. The value of this angle is determined by the method of tilting to be investigated and its values will be respectively $\pi/2$, zero or intermediate for the methods I, II or III described above. The relation between the polar coordinates ϕ and β of the ray seen by an observer at an elevation γ may be reduced to

$$\sin \gamma = \sin \beta \cos \delta + \sin \delta \cos \beta \sin (\phi + \alpha) \quad \dots\dots(8).$$

Assuming β to be small, we may write $\cos \beta$ as unity and the combination of equations (4a) and (8) will lead to

$$\sin (\phi + \alpha) = \sin \gamma \sin \delta + \cos \gamma \cos \delta \sin \theta \quad \dots\dots(9).$$

Less error is introduced in solving this equation from 4-figure tables than in solving equation (8).

Equation (7) describes the polar distribution of intensity and equation (9) gives the relation between the position of the observer in space and his position relative to the polar coordinates of the beam, so it is now possible to write down the intensity which he receives under any conditions. The equations are capable of exact solution but this is laborious and, in view of the approximate nature of equation (7), it is preferable to use a tabular method of solution. An abbreviated example of the calculation for the cosine distribution for a beam tilted by method III is shown in the appendix, the family of curves plotted from it being shown as figure 4c. The order adopted for the solution of the equations has been first to choose a value for δ and to solve equation (4a) for β at integral values of θ and γ . All values of β greater than a chosen value of B are neglected, and the limiting values of θ where $\beta = B$ give the flash-duration at each value of the elevation γ . The second stage has been to solve equation (9) for ϕ over the range of θ appropriate to each value of γ , and with the chosen value of α to represent the method of tilting. Finally, the above values of β and ϕ are inserted in equation (7) to give the intensity seen by a pilot under the conditions corresponding to the chosen values of θ , γ , δ and α . By plotting this intensity against θ at each value of γ , a family of curves is obtained for each case of δ and α , representing both the distribution of intensity throughout the duration of each flash and also the flashing character of the beacon at the various angles of elevation. The case worked out in the appendix and figure 4c is for method III where $\alpha = \pi/6$, the beam is elevated to $\delta = 20^\circ$, and the value of the semi-

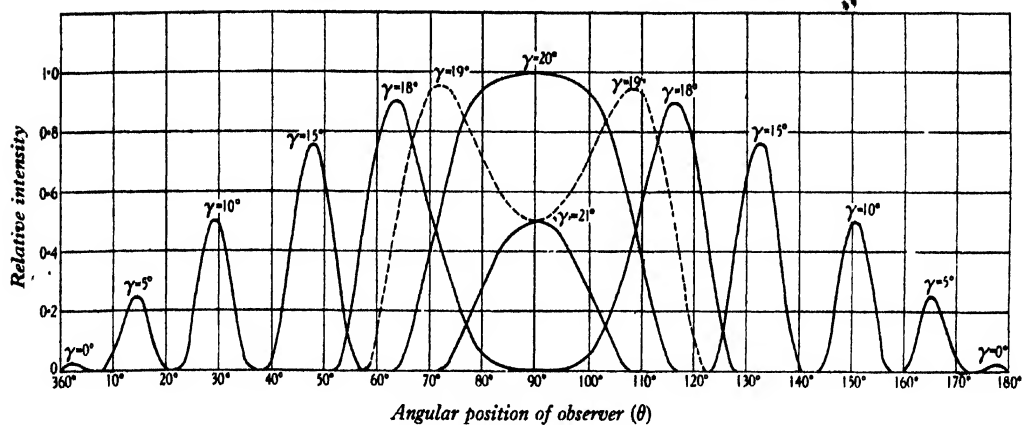


Figure 4 a. Distribution of intensity during flash received by observer. Method I.
Elevation of observer γ ; angle of tilt $\delta=20^\circ$; direction of peak $\alpha=\pi/2$.

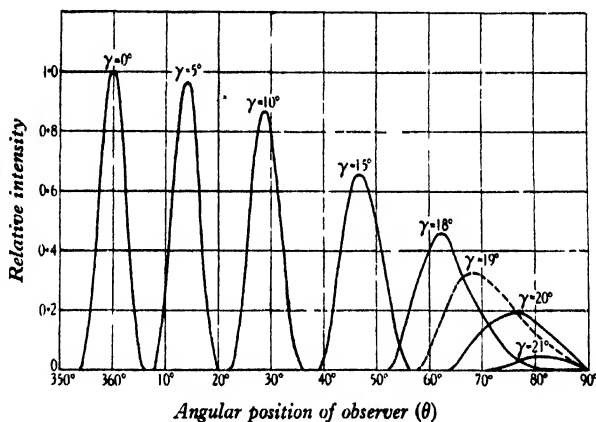


Figure 4 b. Distribution of intensity during flash received by observer. Method II.
Elevation of observer γ ; angle of tilt $\delta=20^\circ$; direction of peak $\alpha=0$.

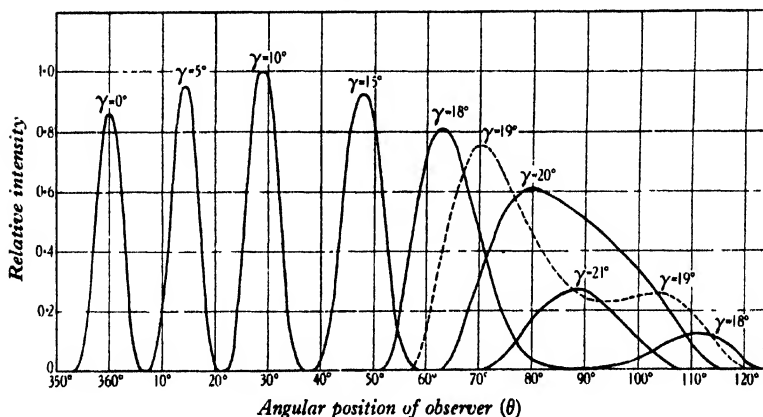


Figure 4 c. Distribution of intensity during flash received by observer. Method III.
Elevation of observer γ ; angle of tilt $\delta=20^\circ$; direction of peak $\alpha=\pi/6$.

divergence B in equation (7) is 2° . Figures 4*a* and 4*b* show the cosine distribution for a beam tilted to $\delta = 20^\circ$ by methods I and II respectively.

Even these families of curves are somewhat complex for ready visualization of the merits of the different methods of tilting, and a further stage has been to summarize them by plotting the peak intensity in flash I' against the observer's elevation

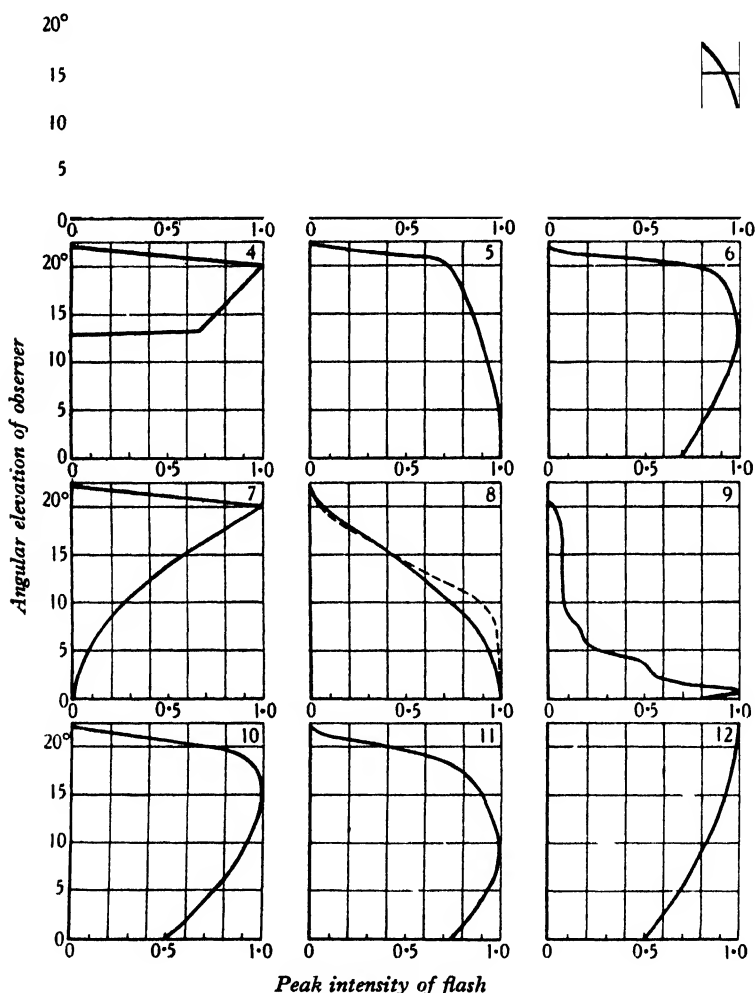


Figure 5. Peak intensity of flash and angular elevation of observer. The broken line gives the distribution for a 9-kw. mirror floodlight.

γ for each case determined by δ and α . This has been done in figure 5, in which the top line gives the summaries for figures 4*a*, 4*b* and 4*c*. These curves can be compared with the theoretical intensity-distribution described in paragraph (a) at the end of the introduction and shown as no. 9 on figure 5. The comparison of each case with the requirement (b) can be made by plotting flash-duration $\Delta\theta$ against elevation γ for each method of tilting as in figure 6.

It will be obvious that the effectiveness of a flash received by the observer will be determined by more factors than just the peak intensity and the gross duration. For a short flash the intensity is integrated by the eye over the duration of the flash, but knowledge of the mechanism of this integration is insufficient to enable us to

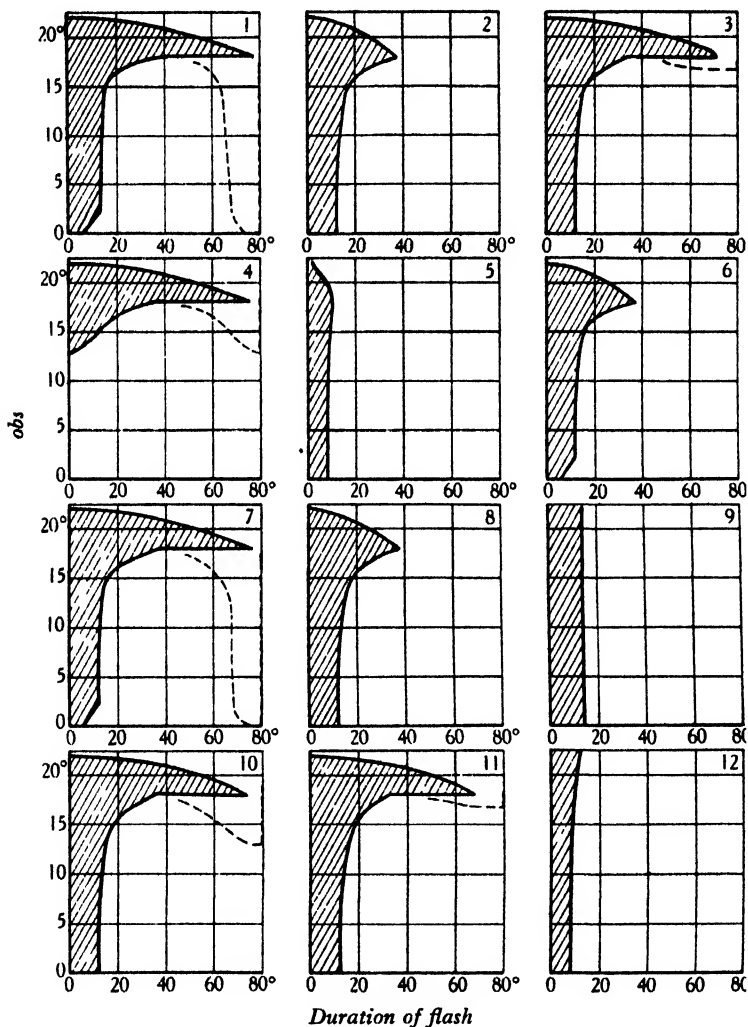


Figure 6. Duration of flash and angular elevation of observer.

carry the analysis to that stage. The effect of flashes which commence and end abruptly is known⁽¹⁾ for a range of illuminations from the threshold up to comparatively high levels, and van Vloten⁽²⁾ has derived a method of integrating flashes which have a trapezoidal distribution of intensity. It is, however, customary to describe a flash in terms of its peak intensity and of its gross duration, and this description is therefore retained in the present paper.

§ 5. RESULTS OF ANALYSIS

Calculations have been made of the distribution of intensity in a number of typical cases with the numerical values shown in table 1.

Table 1

δ (deg.)	20, 30
α (rad.)	0, $\pi/6$, $\pi/4$, $\pi/2$
γ (deg.)	0, 5, 10, 15, 18, 19, 20, 21, 22
B (deg.)	± 2
θ	Integral values from -5° to 185°

In addition to the various possible combinations of numerical values given in table 1, the distribution of intensity has been calculated for floodlights having four different polar distributions. Two of these are represented by equations (7) and (7a) and are called "the cosine distribution" and "the \cos^2 distribution" respectively. The "restricted cosine" distribution is given by equation (7) between narrower limits, and is a representation of a combined mirror and lens floodlight widely used in America. The fourth distribution is shown as a dotted line in figure 2a and represents the 9 kw. mirror floodlight made by the General Electric Company.

It would be wasteful to give the whole of the calculations and results, and typical results are therefore given in the appendix and figures 4a, 4b and 4c. The summarized results for twelve sets of calculations are given diagrammatically in figures 5 and 6, and the conditions for which these figures are drawn are set out in table 2.

Table 2

Method Distribution	I	II	III
Cosine	(1) See figure 4a $\alpha = \pi/2$ $\delta = 20^\circ$	(2) See figure 4b $\alpha = 0$ $\delta = 20^\circ$	(3) See figure 4c $\alpha = \pi/6$ $\delta = 20^\circ$
Restricted cosine	(4) $\alpha = \pi/2$ $\delta = 20^\circ$	(5) $\alpha = 0$ $\delta = 30^\circ$	(6) $\alpha = \pi/4$ $\delta = 20^\circ$
Cosine squared	(7) $\alpha = \pi/2$ $\delta = 20^\circ$	(8) $\alpha = 0$ $\delta = 20^\circ$	(10) $\alpha = \pi/4$ $\delta = 20^\circ$
			(11) $\alpha = \pi/6$ $\delta = 20^\circ$
			(12) $\alpha = \pi/4$ $\delta = 30^\circ$
(9) Air Ministry beacon specification			

The presence of a second flash in each rotation is indicated in figure 6 by the dotted line.

§ 6. DISCUSSION OF RESULTS

The case of method III calculated in the appendix and shown in figure 4*c* may be considered first. An observer at ground level or at any elevation up to rather more than 15° will receive a single flash for each rotation of the beacon, the flash-intensity being within 85 per cent of the maximum and the flash-duration increasing from 12° to 16° of arc. Above 17° elevation, this comparative uniformity of character ceases. From 17° to 18° two consecutive flashes are seen in each rotation, the intensities at 18° elevation being 81 and 13 per cent of the maximum, and the durations 39° and 33° . Above 18° elevation, one long flash (72°) is seen, the intensity and duration both decreasing up to the limit of 22° elevation, above which there is no light.

Figures 4*a* and 4*b* have been plotted from a similar calculation of the intensity-distribution given by tilting the same beam of light by methods I and II respectively. By method I, an observer at ground level will receive two flashes equally spaced during each rotation, but an observer elevated between 0° and 18° will receive two flashes at unequal intervals in each rotation, the difference between the intervals increasing as the elevation increases. The duration of the flashes varies in the same way as for method III described above. At 18° the short interval has become zero and one long flash (72°) is seen, the duration of this flash decreasing to zero at 22° elevation. As regards the peak intensity of the flash, the horizontal intensity is extremely small but the intensity increases proportionately with the observer's elevation up to a maximum intensity at 20° . Above 20° the intensity decreases to zero at 22° .

Method II gives a single flash in each rotation at all elevations, the duration varying from 12° in the horizontal direction to 36° at 18° elevation. The maximum intensity is directed horizontally, and the peak intensity in each flash decreases smoothly to zero as the observer's elevation increases to 22° . The longer durations are associated with lower peak intensities.

The details of the performance described above may be read off the top three diagrams in figures 5 and 6. The diagrams 1, 4 and 7 in these figures all refer to method I and it may be seen that this will always give two flashes irregularly spaced in each rotation of the beacon, with very long single flashes between 18° and 22° elevation. Further, the highest intensities are given at the higher elevations, the horizontal intensity being negligibly small. Both these characteristics are the reverse of the requirements stated in § 1.

Method II is illustrated in diagrams 2, 5 and 8 and will always give a single flash of not greatly varying duration. The highest intensity is directed along the horizontal and the intensity falls progressively to zero at the higher angles. These characteristics are both in accordance with the original requirements, but the method has the disadvantage that as the beam from a floodlight is usually symmetrical, one-half of the light is directed on to the ground when the beam is tilted.

Method III endeavours to overcome this disadvantage by tilting the floodlight about some intermediate axis, so that the peak intensity is directed above the

horizontal and less light is therefore lost. It is illustrated in diagrams 3, 6, 10, 11 and 12, and in general there are two flashes in each rotation at the higher elevations, one flash being of low intensity as in figure 4c. The intensity of the main flash increases as the elevation of the observer increases to some small angle, above which the intensity diminishes to zero at the limit of 22° elevation, with the exception of the case in diagram 12 of figures 5 and 6, which shows the state of affairs for a 30° tilt. Thus the result of saving light is to introduce some degree of irregularity into both the character and the intensity of the flash.

Figures 5 and 6 show that the difference between the cosine distribution and the \cos^2 distribution is a matter of intensity only. The flashing character is exactly the same and both show similar double flashes when the beam is tilted by methods I and III. The difference in intensity-distribution is most apparent when the beam is tilted by method I, but is not sufficient to be of practical importance. Other distributions which lie between these two, such as the G.E.C. 9 kw. mirror floodlight represented by the broken line in figure 5, will give similar results.

It appears then that method II is the one which gives closest adherence to the original requirements. The distribution which is essential for the operation of a projector as a floodlight necessitates the use of a wider beam than that required if the projector is operated as a beacon, and no method of tilting can redistribute the whole of the light in the beam to its best advantage. The essential difference between methods II and III is that the former puts the excess light into the ground while the latter puts it into the higher angles, where it is not necessarily of practical value. It should be noted that method III would be suitable to a system having a narrow beam-spread, and the analysis outlined above enables one to calculate the characteristics of any given beam when tilted.

§7. ACKNOWLEDGEMENTS

We are indebted to the General Electric Company for the data shown as the dotted curves in figures 2a and 5.

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DISCUSSION

Dr W. S. STILES enquired whether the methods to which figure 6 relates have been tested in practice, with results in accordance with the theory.

AUTHOR'S reply. The three methods described have all been used in full-scale apparatus and observation has verified the calculations of flash-duration. The only way of obtaining the effective flash-intensity is to integrate the distribution of light

in the flash by an empirical point-by-point method, which leads to a factor of the type $t/(a+t)$, where t is a measure of the duration and a is a constant depending on the intensity of illumination. The values of a are known for abrupt and for trapezoidal distributions, and the peak intensity is multiplied by this factor to give the effective intensity from which the range of the beacon can be calculated. For gradual distributions, such as are found in practice, the values of a are in general larger than for trapezoidal distributions of the same total duration, and the effective intensity is accordingly less. If the flash-duration is deliberately increased by defocusing the lamp, or by some similar method, the peak intensity is decreased proportionately and the effective intensity will be decreased slightly. It is therefore desirable in practice to have a flash as short and as intense as possible, with the intensity rising and falling sharply at each end.

APPENDIX

Cosine distribution. Beam tilted by method

 $\pi/6$ 20°

θ (deg.)	Values of γ							
	0°		10°		18°		20°	
	β (min.)	ϕ (deg.)	I	β (min.)	ϕ (deg.)	I	β (min.)	ϕ (deg.)
-2	41	-31.9	0.629	108	-5.1	0.024		
0	0	-30.0	0.866	71	-3.2	0.356		
2	-41	-28.2	0.653	-18	1.5	0.945		
4	-82	-26.2	0.205	-102	6.2	0.053		
23								
25								
30								
35								
55								
60				82	26.8	0.203		
65				30	31.6	0.719		
70				-16	36.3	0.770		
75				-53	41.0	0.446		
80				-80	45.6	0.174		
85				-103	50.3	0.032		
90				-116	55.2	0.001		
95				-120	60.0	0.000		
100				-116	64.8	0.001		
105				-103	69.7	0.017		
110				-80	74.4	0.099		
115				-53	79.0	0.112		
120				-16	83.7	0.070		
125				30	88.4	0.018		
130				82	—	—		
Duration of flash	12°			14°			52°	36°
Peak intensity of flash	0.866			1.000			0.610	0.262

THE MUTUAL SHUNT METHOD OF MEASURING SELF INDUCTANCE AT RADIO FREQUENCIES

By ALBERT CAMPBELL, M.A.

Received 25 March 1938. Read 10 June 1938

ABSTRACT. A simple method of measuring self inductance is described, in which the value is read directly on a mutual inductometer. Its secondary circuit, with an a.-c. ammeter in series, is put in parallel with the coil to be tested, the combination being connected, thro' the primary coil, to an a.-c. source of radio frequency giving constant current. The mutual inductance is now varied until the ammeter reads a minimum current, and then the self inductance is equal to the mutual inductance. This result does not involve resistance or frequency. Methods for eliminating the errors due to self and mutual capacitances in the inductometer are indicated.

§ 1. INTRODUCTION

FOR the measurement of self inductance at radio frequencies the most accurate methods are those in which resonance with a standard capacitor is used. These resonance methods are not always convenient, however, particularly when small inductances are to be measured over wide ranges of frequency. The null bridge methods, so useful at the lower frequencies, are not easy at radio frequencies, for the simpler current-measuring instruments (such as galvanometers with thermal converters or rectifiers) are mostly of square-law type and are very insensitive near zero reading. Thus for null methods more elaborate detectors have to be used.

§ 2. DESCRIPTION OF METHOD

I have recently devised a direct-reading system which quite avoids this difficulty. It is shown in the figure, where B , the coil to be tested, has resistance R and self inductance L .

In parallel with B there is an a.-c. ammeter A in series with the secondary coil of a mutual inductometer in which the mutual inductance M can be varied over a long range. The radio-frequency source is connected thro' the primary circuit of M as shown, with the point E earthed.

Let r and l be the total resistance and self inductance of the secondary branch, and i and i_2 the instantaneous values of the alternating currents as in figure 1, with effective values I and I_2 . Then the current in B will be $(i - i_2)$, and if the a.c. is purely sinoidal and of pulsance ω , we have

$$(R + Lj\omega)(i - i_2) = (r + lj\omega)i_2 \pm Mj\omega i$$

or

$$[R + r + (L + l)j\omega]i_2 = [R + (L \pm M)j\omega]i.$$

Taking the minus sign for M , we have

$$\frac{I_2^2}{I^2} = \frac{R^2 + (L - M)^2 \omega^2}{(R + r)^2 + (L + l)^2 \omega^2} \quad \dots\dots(1).$$

Now if I is kept constant and M alone is varied, when the current I_2 shown by the ammeter is a minimum,

$$L = M \quad \dots\dots(2).$$

Thus L is measured directly, and the result does not involve the frequency or the resistance R of the coil.

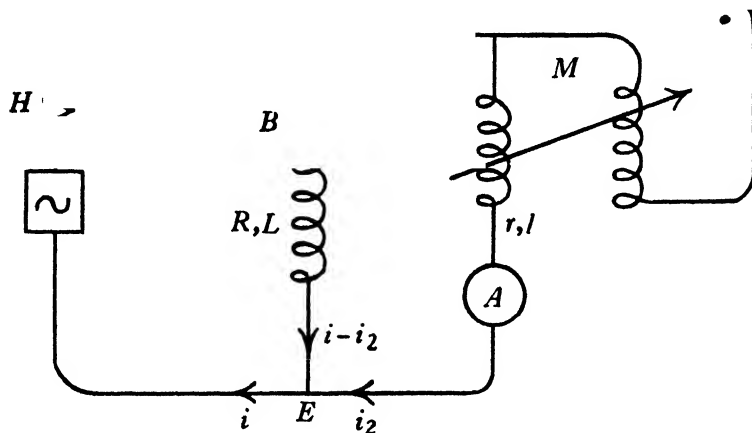


Figure 1.

It is best to obtain M by taking the mean of two values, above and below M , which give equal values of I_2 . There is no need to know the calibration of the ammeter, and its scale may follow any law. As the result is independent of frequency, the wave form may contain harmonics. To ensure that I shall remain constant while M is varied, the outer circuit must contain impedance (as at H) much greater than that of the working part. The system may conveniently be named the "mutual shunt method".

It will be noticed that by reversing the connexions of one of the inductometer coils (i.e. changing the sign of M) negative self inductances can be measured over the same range.

§ 3. CORRECTION OF ERRORS DUE TO CAPACITANCES OF COILS

The simple theory just given becomes more complicated when the mutual inductance is not perfect, and the result obtained is affected by errors due to the self capacitances C_1 and C_2 and the mutual capacitance K of the primary and secondary coils of the varinductor used. As Butterworth⁽¹⁾ has shown, part of the total error increases with frequency, being proportional to ω^2 . Moreover, when $L=0$ there is a zero error which increases with frequency. The errors become

worse as the maximum range of M is increased. In the present application K usually causes more error than C_1 and C_2 .

To get over these troubles I have constructed inductometers with relatively small self and mutual capacitances (by using single-layer coils and the like), and containing compensating systems to reduce the errors. The zero error can be largely reduced by putting in series with the L coil a resistance shunted by a capacitance and resistance in series. The remaining error, which varies as the reading of M is altered, is reduced by adding a closed tertiary circuit coupled to the primary and secondary circuits^(a). Compensation can be obtained by proper choice of ρ , the resistance, and λ , the self inductance, of this auxiliary circuit. For small errors the compensation will hold over a good range of radio frequency, but in the more extreme cases it may be necessary to reset ρ for each frequency used. In the latter case it is necessary to know the frequency approximately.

§ 4. ACTUAL APPARATUS

I have constructed a number of inductometers of various ranges from 0 up to 300 $\mu\text{H.}$, all meant to work up to frequencies of 800 kc./sec. and even higher. These instruments had their scales marked at 50 c./sec., and were adjusted to give minimum errors when testing L coils checked by the National Physical Laboratory or coils of calculable self inductance. For the complete set-up the a.-c. source is an oscillator with a single small valve (with filament current 0.075 amp., and anode voltage 120 v.), giving a variety of frequencies from 10 kc./sec. up to 800 kc./sec. The output coil can be turned so as to vary the coupling from 0 to the maximum; this is useful to prevent overloading the ammeter. For the ammeter a thermal converter (heater and thermojunction) was used at first, but for better sensitivity this was replaced by a small transformer connected to a full-wave copper-oxide rectifier and a moving-coil galvanometer. By the use of a Spot galvanometer (made by the Cambridge Instrument Company) the whole apparatus is made completely portable; it occupies very little space and can be run by dry cells.

§ 5. RESULTS

The following three examples illustrate the kind of results obtained:

Model	Range ($\mu\text{H.}$)
No. 1	-0.1 to +1.25
No. 2	-0.4 to +13
No. 3	-12 to 300

In each case the small residual zero errors were allowed for.

No. 1 could be read to 0.002 $\mu\text{H.}$ even at the higher values. Without compensation it appeared to have very little error and no variation with frequency up to 800 kc./sec.

In No. 2, which was the one chiefly studied, the added compensations were quite automatic and reduced the error to less than 0.05 $\mu\text{H.}$ at all points of the scale (e.g. less than 0.4 per cent at the top reading).

No. 3 without compensation showed a maximum error of about 30 per cent at 800 kc./sec. In its tertiary circuit a rheostat was arranged to be set at the proper resistance for each particular frequency. In this way the error was reduced to less than $2\mu\text{H.}$ at all points of the scale.

When R is very large in comparison with $L\omega$ or $l\omega$, large errors may arise. Such extreme cases, which are not common in practice, cannot be dealt with by this method.

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- (1) BUTTERWORTH, S. *Proc. Phys. Soc.* **33**, 312 (1921).
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DISCUSSION

MR R. APPLEYARD. It is pleasant to realize that the problem of determining mutual inductance continues to engage the attention of electricians in this country, where it may be said to have had its origin. It is cheering, too, for us to remember that it has been intimately associated with the Physical Society. The account given to the Physical Society on November 27, 1886, by Professor G. Carey Foster, of a method of determining what was then a very elusive quantity gave the impetus to the investigation. At that time, it was thought likely that it would be of service in the design of dynamo-electric machinery. Between the years 1900 and 1907, when the work of Oliver Heaviside began to be appreciated and to yield tangible results, mutual inductance had to be measured in the factories—a laborious yet fascinating task. It remained fascinating, but it became far less laborious when, after the achievements of Heaviside and of Lord Rayleigh, the author placed in our hands his masterpiece, the inductometer. It was with this instrument that electricians were able to solve many of the practical difficulties in the design of loaded telegraph and telephone cables. He now presents them with means to measure small inductances at radio frequencies, and he deserves their gratitude. It is likely also that the instrument may prove of benefit when measurements have to be made in some of the subtle cases that arise in interference problems in telephony, where the quantities to be detected and gauged are next to nothing.

Telephone engineers are to-day concerned with mutual inductances of the order $1\text{ m}\mu\text{H.}$ (10^{-9} henry). They may require to know whether the inductance between two circuits is say 1, 2, 3, . . . , 10, . . . , 100 such units, to an accuracy within say $\frac{1}{2}$ or 1 unit. The range of frequency in these cases may be from 5000 c./sec. to 60,000 c./sec. The currents, where these mutual actions have to be determined, may be too small to be detected by a telephone. An amplifying system has therefore to be adopted.

DR L. HARTSHORN. Mutual inductometers were first devised by the author nearly thirty years ago, and they have been standard laboratory instruments ever

since. It is remarkable that Mr Campbell should at this stage be able to describe an application of the instruments which is novel and yet so beautifully simple. The single adjustment, and the lack of dependence of the readings on resistance or, to a first order of approximation, on frequency, are valuable features of the method for general testing purposes.

In connexion with the greater sensitivity obtained by the author with this method than with null bridge methods, it is interesting to note that for a coil of negligible resistance it becomes a null method. The curve connecting instrument reading and galvanometer deflection is rather like a resonance curve, which becomes flatter the higher the value of R . Thus although an increase of R tends to increase the sensitivity inasmuch as it causes the detector to operate at a more sensitive point on its characteristic curve, it also tends to diminish the sensitivity by flattening the response curve of the instrument. There is presumably an optimum condition for sensitivity, and it seems likely that it might be near the conditions obtained in the ordinary use of this instrument on typical coils.

At first sight it appears as if the self capacitance of the coil under test being added to that of the secondary coil of the inductometer must modify its calibration at the higher frequencies. In practice the compensating system would presumably be adjusted with a coil of known self capacitance in circuit. If the compensating circuit were set so that the values obtained by measurements on the standard coil included the effect of its self capacitance, then the instrument would subsequently give correctly the effective series inductance L_1 of any coil. If, however, the compensating circuit were set so that the values obtained for the standard coil excluded the effect of its self capacitance C , then the instrument would subsequently give the equivalent shunt inductance L_2 of a coil provided its self capacitance were equal to that of the standard. It is well known that $L_1 \div L_2 / (1 - L_2 C \omega^2)$. The instrument would probably be used for measurements in which such differences are not important, but it is interesting to note that for routine tests on similar coils the compensating circuit could be adjusted so that the reading of the instrument would give either L_1 or L_2 .

The use of a transformer and copper-oxide rectifier as a sensitive ammeter at such high frequencies is interesting. A thermal instrument would probably be much less satisfactory owing to its inability to stand the overloading which would be likely to occur in routine testing. Is the transformer of special design?

Dr D. OWEN. The author's name is closely associated with the mutual inductometer, both in its development as an instrument of precision and in the devising of various new methods of measurement involving its aid. He now extends its application to very high frequencies, and the present communication embodies a simple method for the measurement of self inductance.

One or two questions suggest themselves. It would be of interest to know to what sources the zero error is to be assigned. The absence of any reference to the self capacity of the coil under test is noticeable; it is difficult to see how this useful datum is to be obtained by measurements at a single frequency. Again, the models

no. 1 and no. 2 are designed to deal with self inductances of the small values which would be required normally for use at frequencies far above 800 kc./sec. On the face of it, this would appear to discount the value of the method as applied to short-wave coils.

AUTHOR'S REPLY. Mr Appleyard rightly points out the importance of Prof. Carey Foster's work. The Carey Foster bridge is still the simplest and best method of determining capacitance in terms of mutual inductance.

Dr Hartshorn notices that, for a given value of L , there should be an optimum value of R to give the best sensitivity. For this reason there is permanently mounted in the inductometer a resistance, for connection in series with the unknown coil, of such a value as to give satisfactory sensitivity for the whole range of M from 0 to the maximum, and over the whole working range of frequency.

The mutual shunt system can be worked as a null method, if desired, by making the closed tertiary circuit ρ , λ completely adjustable. If it is coupled to the primary and secondary circuits by mutual inductances m and μ respectively, then by adjustment of ρ , λ , m and for μ the current in the detector can be brought to zero, in which case

$$R = \frac{m\mu\lambda\omega^2}{\rho^2 + \lambda^2\omega^2} \quad \text{and} \quad L = M + \frac{m\mu\rho}{\rho^2 + \lambda^2\omega^2}.$$

If ρ can be made very small compared with $\lambda\omega$, these equations become much simpler, and it is possible that this null method might be useful in certain cases.

The inductometer is usually compensated so as to give the series L_1 of the coil under test. If L_2 is appreciably constant for the frequency range, it can be deduced by observing L_1 at two frequencies.

With regard to the sensitive detector used, I have to thank Mr W. L. Beck for kindly suggesting the use of a transformer in front of the rectifier. The transformer is of his design, with a closed magnetic circuit of mumetal.

In reply to Dr Owen: Butterworth's formula* does not perhaps quite meet the case, but it indicates that the zero error is due to the mutual capacitance between the primary and secondary coils. The method cannot determine the self capacitance of an unknown coil by a single reading at one frequency. By testing short-wave coils standardized by other methods, the models no. 1 and no. 2 might be compensated to read L_1 correctly at frequencies much higher than 800 kc./sec. Model no. 1 (to $1.2\mu\text{H.}$) would probably be satisfactory up to 8000 kc./sec., but it is hard to predict without sufficient experimental foundation.

* *Proc. Phys. Soc.* **33**, 312 (1921).

ANOMALOUS TRICHROMATISM AND ITS RELATION TO NORMAL TRICHROMATISM

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Imperial College of Science and Technology

Communicated by Dr W. D. Wright, 5 October 1937. Read 2 June 1938

ABSTRACT. The characteristics of six deuteranomalous observers and one protanomalous observer have been examined. In the case of the former it has been shown that, in contrast with what occurs in normal trichromatism and dichromatism, it is not possible to take mean values as representative of the deuteranomalous observer. This fact, combined with the results of the statistical survey with the Nagel anomaloscope, suggests that anomalous trichromatism is an intermediate state between dichromatism and normal trichromatism. In the case of the protanomalous this transition would seem to be of a continuous nature, but for the deuteranomalous there is a subsidiary maximum in the distribution curve.

§ 1. INTRODUCTION

IT has been found by experiment that the majority of colours can be matched for the normal person by a mixture of red, green, and blue; and further, it has been shown that any colour quality can be uniquely expressed by an equation of the type

$$C = aR + bG + cB \quad \dots\dots(1),$$

where C is the colour quality, R , G and B the primary colours to be mixed, and a , b and c the proportions of the three primary colours, such that

$$a + b + c = 1 \quad \dots\dots(2).$$

While the equation (1) will hold in all cases, it is found that some observers need have only two primary colours in order to match all other colours, and for others that only one primary is needed.

It can therefore be said that the colour-vision of all types of observers can be divided into three main groups, according as it is a function of one, two, or three variables. These three main groups are known as monochromats, dichromats and trichromats respectively. But although this classification is fundamental, there may be border-line cases.

In the investigation of the properties of the various types of colour-vision it has been found necessary to subdivide the main groups further. The first type, namely the monochromats, have not been further subdivided; while in their case there may be no more than one type of luminosity curve, no subdivision is possible from considerations of colour. The dichromats can be divided into three distinct classes; various names have been applied to them, but the most common are those introduced by von Kries, and since he introduced them so as to be independent of any

theory, they will be used throughout this paper and assumed to have no theoretical significance. The classes of dichromats are protanopes, deuteranopes and tritanopes. Both the protanopes and deuteranopes are unable to distinguish colour-differences in the red-green region of the spectrum, and the tritanopes in the blue-green region of the spectrum; these last are rare. The former two types are defined by comparison of their luminosity curves with the normal. The protanopes are defined as having the maxima of their luminosity curves displaced towards the blue, while those of the deuteranopes are displaced towards the red, relative to the normal⁽¹⁾.

In the case of the trichromats there are two main classes, known as normal trichromats, to which class the majority of observers belong, and anomalous trichromats, who were first distinguished from the normal by Lord Rayleigh⁽²⁾, who showed that in matching a yellow with a mixture of red and green the anomalous observer required more of either red or green than the normal to make a match. This latter class may again be subdivided and, as with the dichromats, the names to be given to the subdivisions are a subject for controversy. For the sake of uniformity of language, and since the names are already in use, the names protanomalous, deuteranomalous and tritanomalous will be used to distinguish the classes of anomalous trichromat. The definitions of these types are made from the region of the spectrum in which they are anomalous and from their luminosity curves in the same way as for the dichromats. But beyond this similarity of name and definition no further connexion with the dichromats is necessarily implied by the use of the names.

It is with anomalous trichromatism that this paper as a sequel to F. H. G. Pitt's work on dichromatism⁽¹⁾ is concerned. As yet the colour characteristics of anomalous trichromatic vision have not been fully investigated, and in consequence any physiological analysis must necessarily have been of a very speculative nature. The detailed characteristics of several anomalous observers are here given and an attempt has been made to relate the different types of colour-vision to one another. A statistical survey of a number of observers chosen at random has also been carried out, to discover where the observers whose characteristics have been determined came in relation to other observers, and to ensure that all the observers chosen were not of the same type.

§ 2. APPARATUS AND METHOD

The apparatus used was the Wright colorimeter⁽³⁾, which is described elsewhere.

The procedure adopted in using the apparatus is as follows. One half of the field is filled with light from the test colour, and the other half with a mixture of light from the three primaries. A match is obtained for both colour and intensity by the observer's suitably adjusting the amount of red, green, and blue by means of the photometer wedges. In order that the observer may give an accurate match, he should keep looking away and looking back to rest his eyes. All measurements were taken in a darkened room, and after the observer had been dark-adapted for at least ten minutes. This period of dark-adaptation is to allow the observer to settle down and to give his eyes a preliminary rest; it is not an attempt to obtain a match

in the dark-adapted state. Actually the final match is the same whether the observer has been dark-adapted for the full period of half an hour, or has been light-adapted, provided that the intensity of light-adaptation is not too high.

With the above arrangement the following characteristics for any observer may be determined: (1) the spectral coefficients, (2) luminosity and mixture curves, and (3) hue-discrimination data.

To determine the saturation-discrimination by adding small quantities of spectral colour to white, it is necessary to make some additions to the above apparatus. A diagram of the essential parts is shown in figure 1; a brass sector S , coated with magnesium oxide, is illuminated by light from a lamp as specified for the C.I.E. 1931 Standard Illuminant B⁽⁴⁾. The sector is so arranged that both halves of the photometric field in the prism P are filled during one half of the revolution; and during the other half of the revolution monochromatic radiation of known wave-length is admitted to the top half of the field. This monochromatic radiation is obtained from the spectrum W_2 , and the intensity is controlled by means of a calibrated photometer wedge. The intensity of the white S_B in the top half of the

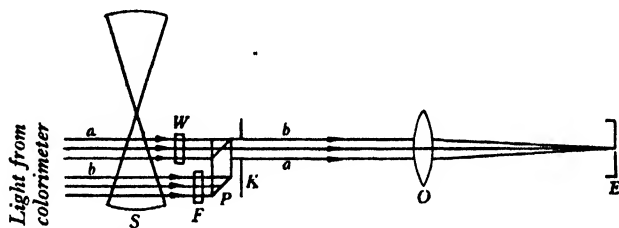


Figure 1. Diagram of optical system for saturation-discrimination.

field may be controlled by neutral filters F , but it is advisable to use only the lightest filters, as the darker ones deviate considerably from neutrality. In the lower half of the field the intensity of the white is controlled by a very shallow photometer wedge. It is necessary to have the white of one half of the field so arranged that it can be varied continuously in intensity, and the use of a shallow wedge is probably the most satisfactory, as the deviation from neutrality would be negligible. The sector can be run at two speeds, fast to remove flicker between the white of the top half of the field and the monochromatic radiation, so that a discrimination step can be made between the mixture and the pure white in the lower half of the field; and slow, so that the intensities of the white and the monochromatic radiation may be compared by flicker.

For the statistical survey the Ishihara cards were used as a purely qualitative test, to determine whether the observer was deficient in colour sensitivity.

To divide the observers into their distinctive classes the Nagel anomaloscope was used. In this instrument one half of a photometric field is filled with monochromatic yellow, and the other with a mixture of monochromatic red and green. The intensity of the yellow is variable and also the ratio of red to green in the mixture, and thus it is possible to match the two halves of the field in colour and intensity. The instrument is calibrated so that for any observer the ratio of red to

green required for the match can be found. Since it is possible to vary the red-to-green ratio from zero to infinity, it is possible, in the case of dichromats, to find the relative luminosity of the red and the green by matching each in turn with the yellow, and since it can be seen from their luminosity curves⁽¹⁾ that L_R/L_G for protanopes will be much less than L_R/L_G for deuteranopes, it is possible to distinguish between them.

The wave-lengths used for the red, yellow, and green were 0.650, 0.578 and 0.535 μ . respectively. In the case of the yellow it is usual to use 0.589 μ ., and it is convenient to examine the relative advantages of setting the yellow of the anomaloscope at 0.578 μ . and 0.589 μ . respectively. In connexion with hue-discrimination the latter would have an advantage, but this would not be very large. On the other hand, in any one instrument the values of the wave-lengths for the red, yellow and green are all interdependent, and changing the yellow from 0.578 to 0.589 would cause a corresponding change in the red and green wave-lengths, but from the hue-discrimination curves it can be seen that this change would decrease the number of steps, and thus the difference in colour, between the red and the green. This would tend to make the settings less accurate. Thus it is probable that there is very little difference in the accuracy obtained by using one wave-length and the other. In order to test this conclusion, about 15 observers, both normal and deuteranomalous, were asked to make matches on the colorimeter, using the instrument primaries and a test-colour at 0.589 μ . The results obtained showed a very close agreement with those obtained from the anomaloscope.

The white used throughout was the Standard Illuminant B set up by the C.I.E. in 1931⁽⁴⁾.

§ 3. UNITS AND METHODS OF EXPRESSING RESULTS

The trichromatic units have been based on two monochromatic matches, as in the W.D.W. system of units⁽⁵⁾, but the same unit colours have not been used. In the W.D.W. system the units were based on matches at 0.5825 and 0.4940 μ ., at which the red and green and the blue and green coefficients respectively are made equal. The advantage of this system for the purpose of research is that the resulting spectral coefficients will be independent of the macular pigmentation of the observer's eye, which makes it possible to eliminate one of the variables in an analysis of the curves. Moreover in the case of a normal observer the position of the white point will indicate the extent of the pigmentation. It was found that if the W.D.W. system were used to express the coefficients of a deuteranomalous observer, the negative red coefficients in the blue-green region of the spectrum would be very large and uncertain, and, while there is no objection to their being large, the uncertainty would directly influence the blue and green coefficients. It was therefore decided to reduce the values of the negative red in such a way as to reduce this uncertainty, but at the same time to keep the values large enough for comparison to be made between the results obtained by different observers. For this purpose a new unit colour was chosen at which to make the red and green coefficients equal, the other unit colour being the same as in the W.D.W. system. This new colour

was at 0.6100μ . for the deuteranomalous observers, and for convenience the system will be known as the J. H. N. (1) system of units.

In the case of protanomalous observers the negative red coefficients become inconveniently small when the W. D. W. system is used. In this case it is not convenient to move the unit colour to the region of 0.57μ ., since in this region the hue-discrimination is very poor, but precisely the same effect can be obtained by using 0.6100μ . and making the ratio of the red-to-the green coefficient be as 10 is to 1. The other unit colour is again the same as in the W. D. W. system. This system will be known as the J. H. N. (2) system of units.

It is convenient to summarize these systems of units in tabular form, since the two types of anomalous trichromats have their final results expressed in two different ways, rendering direct comparison of their spectral coefficients impossible. They may, however, be compared with the normal observer's results expressed in their respective systems.

Table 1. Unit colours

	W. D. W. (μ .)	J. H. N. (1) (μ .)	J. H. N. (2) (μ .)
$R=G$ }	0.5825	0.6100	—
10 $G=R$ }	—	—	0.6100
$B=G$	0.4940	0.4940	0.4940
Primaries R	0.6500	0.6500	0.6500
G	0.5300	0.5300	0.5300
B	0.4600	0.4600	0.4600

The luminosity curves are expressed in relation to the point of maximum luminosity, which in each case is made equal to unity. The results for all observers are thus comparable. The luminosity curves, which are for an equal-energy spectrum, are also split up into their three components, showing the relative luminosities of the red, green, and blue primaries needed to match each point of the spectrum. These and the subsequent curves are directly comparable with the corresponding normal curves.

The hue-discrimination is expressed as the least noticeable difference in wavelength at each point in the spectrum, when the intensities of the test and comparison fields are kept equal throughout the observation.

The saturation-discrimination is determined by finding the just noticeable difference in saturation from the white point S_B . If L_S is the intensity of any wavelength that has to be mixed with L_W , the intensity of S_B to produce a just noticeable difference, then the saturation-discrimination is expressed as the logarithm of the ratio $(L_W + L_S)/L_S$. A large value of this expression indicates a highly saturated spectral colour.

§ 4. STATISTICAL SURVEY AND RESULTS

In the statistical survey the observer was first asked to read the Ishihara cards, and any mistakes or hesitation were noted. In this way it was almost always possible to detect any deficiency, but only in a general way, dividing the observers into normal

and abnormal. After they had read the cards all observers were asked to make a match on the Nagel anomaloscope. As only one match was taken, the observer was asked to look away at a dark card, and look back at the match once or twice, in order to make sure that the match was as accurate as possible. In the case of normal observers, some of whom repeated their readings after long intervals, it was found that this method gave results accurate to within about one scale division, while if a number of matches were taken by one observer the variation was between a half and one scale division. These figures may be compared with the variation of eight scale divisions between different normal observers. In the case of the anomalous trichromats the settings were not so exact, but as will be seen later from the hue-discrimination curves it would not be reasonable to expect the same accuracy.

The readings for the dichromats, which were used only for purposes of classification, were obtained by asking the observer to make two intensity matches, one between yellow and red and the other between yellow and green⁽¹⁾.

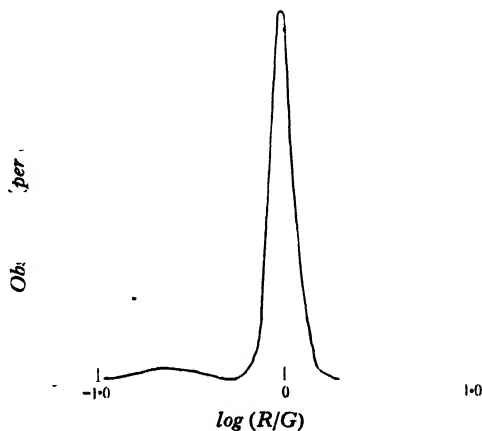


Figure 2. Distribution of R/G ratio for Nagel match.

The results of the survey are shown in table 2 as percentages of colour-defectives, and also in the form of a curve, figure 2, the ordinates of which represent the logarithm of the ratio of red to green in the match obtained, while the abscissae represent the percentage of observers giving that ratio. The ratio of red to green, by which the results are expressed, is comparable but not identical with the *Anomalquotient* introduced by Trendelenburg⁽⁶⁾. In a general way the results obtained by the author agree with those obtained by Schmidt⁽⁷⁾, as to the nature of the distribution of the anomalous trichromats. However, the latter finds a gap between the red-to-green ratio for the normal and for the deuteranomalous observers, while the author's results show only a dip in the distribution curve.

The results obtained for the percentages of various forms of colour-deficients are, as can be seen in table 2, somewhat higher than those obtained by other workers. Schmidt criticizes her own results as being too low since, as the readings were taken at a public exhibition, those who knew of their defect did not wish to

show it. Some of the author's results were taken at the Physical Society's exhibition, where it was found that those who knew of their defect made a special point of presenting themselves.

Table 2. Results of statistical survey (males)

	Author	Schmidt ⁽⁷⁾	Waler ⁽¹¹⁾	v. Planta ⁽¹²⁾
Total number	1338	6863	9049	2000
Protanopes (per cent)	1.27	1.09	0.88	1.60
Deutanopes (per cent)	1.20	1.97	1.03	1.50
Protanomalous (per cent)	1.27	0.68	1.04	0.60
Deutanomalous (per cent)	5.08	4.01	5.06	4.25
Total deficientes (per cent)	8.82	7.75	8.01	7.95

§ 5. MEASUREMENT OF INDIVIDUAL CHARACTERISTICS

As a preliminary to recording the characteristics of each observer, several colour-matches were taken to accustom the observer to the apparatus; these results were recorded, and when the observer could give consistent results the measurement of the characteristics was started. The agreement to be considered as consistent was by no means the same for each observer, owing both to the variation in their defects and also to their inability to make scientific observations. For this latter reason it was found necessary to discontinue observations in some cases.

The following characteristics were measured for various observers; the exact experimental procedure in each case will be explained: (1) spectral coefficients; (2) equal-energy luminosity and spectral-mixture curves; (3) hue-discrimination; (4) saturation-discrimination; (5) coefficients of C.I.E. 1931 Standard Illuminant B.

(1) The method of basing the trichromatic units has been explained in § 3, the coefficients being based on two monochromatic matches. In practice the observer is asked to match the two unit colours before each set of readings. From these two matches, correction factors are obtained which must be applied to the readings from the photometer wedges controlling the intensities of the primaries in the mixture.

Throughout the readings for the coefficients three observations were taken on each match. In general the observer was asked to upset and reset each primary separately, but in some cases, especially in the yellow region, it was found necessary to ask the observer to upset both red and green primaries together, and to take a mean of more than three settings. In the case of each observer the final curves are a mean of several sets of results.

(2) The same observations were used to calculate both the trichromatic coefficients and the luminosity curves, and for this it was necessary to know the relative luminosities of the instrument primaries. These would, however, depend for their constancy on the condition of the instrument always remaining the same, and so the relative luminosities of the primaries needed to match the unit colours were found in each case, and were a constant for each observer.

This comparison was made by flicker, the apparatus being specially arranged⁽³⁾. When the three primaries had been compared in this way, matches were

made on the two unit colours and so the relative luminosities of the primaries needed for the matches could be calculated. These readings supplied a second correction factor to be applied to the wedge readings, after the application of the trichromatic unit-correction factor; but this factor, being a constant for the observer, could be used throughout the whole series of readings for any observer, any change in the apparatus being allowed for by the trichromatic unit-correction factor.

The luminosity curve given by the above method would refer to a spectrum having a particular energy-distribution depending on the source of light and the apparatus. In practice it is necessary to refer the curve to an equal-energy spectrum, and to do this it is necessary to correct for (1) the variation in the dispersion of the spectrum; (2) the energy-distribution of the source of light; and (3) selective absorption in the apparatus.

These measurements give constants of the apparatus and were originally taken by Pitt⁽¹⁾. As a check these constants were obtained by a slightly different method. To find the dispersion at various points in the spectrum, Pitt's method was to fit a narrow slit in front of the test colour prism, and then, by examining the exit pupil with an eye-piece, to determine the dispersion at various parts of the spectrum. From these readings a curve could be drawn showing the variation of the dispersion with the wave-length. As a check on these measurements the pointolite lamp was replaced by a mercury vapour lamp. The lines emitted could be viewed directly in the exit pupil with an eye-piece without the use of an additional slit in the spectrum, and so the dispersion was measured at the various wave-lengths emitted by the lamp. In the same way a curve was drawn showing the variation of the dispersion with wave-length.

In the case of the second and third corrections, the method adopted by Pitt was to take measurements for several normal observers, and then assuming that the mean point of maximum luminosity for these would be the same as for the C.I.E. 1931 Standard observer, to find the colour temperature of the lamp, assuming the energy-distribution to be Planckian; this made the maximum come to 0.555μ ., the maximum for the standard normal observer.

Owing to the smallness of the quantity of energy actually emitted, any direct measurement of the energy-distribution would be very tedious, if possible with any degree of accuracy. However, if it is assumed that the energy distribution is approximately Planckian when it emerges from the exit pupil, then the effective colour temperature of the source can be measured by measuring the colour obtained by reflecting back the whole of the spectrum W_1 with a white diffusing surface, and matching it with the instrument primaries. For this measurement the units were obtained by a match on the C.I.E. 1931 Standard Illuminant A⁽⁴⁾. From the results of measurements of various colour temperatures, Judd⁽⁸⁾ has drawn a locus in a colour triangle so that, given the colour of a source, its effective temperature can be found. It was found that the colour given by the source lay a little way off the curve for sources of Planckian distribution. The difference from the Planckian distribution, which was small, was assumed to be due to excess absorption of the blue, and so the colour temperature was found by joining the point given by the source to the

blue origin, and the point where this line cuts the locus was taken as the effective colour temperature of the source as seen through the exit pupil. The results obtained by the two methods agreed very closely, the apparent colour temperature being 2600° K. in each case.

By measuring the energy-distribution in this way, both the energy-distribution of the source and the selective absorption in the apparatus can be corrected for at the same time, and with the curve for the variation in dispersion throughout the spectrum the equal-energy luminosity curves can be calculated. Further, the mixture curves can be calculated from the equal-energy luminosity curve, the spectral coefficients, and the relative luminosities of the primaries.

(3) In the measurements of the hue-discrimination it was necessary to fill both halves of the photometric field with light of approximately the same wave-length. To do this, two of the instrument primaries were removed and the third was set to the required wave-length to provide the colour comparison field. The test colour was arranged so that the wave-length could be controlled by the observer. The observer was asked to set the test colour so that there was the smallest distinguishable difference in colour between the two halves of the field, when the intensities were exactly the same. The intensity of the primary was controlled by means of the photometer wedge. In this way it was possible to find the difference limen due to colour alone at various points throughout the spectrum, and thus a curve could be drawn showing the difference limen at any point in the spectrum.

(4) The arrangement of the apparatus for the determination of the saturation-discrimination has been described in § 2. The test colour was removed and one of the primaries was set to the required wave-length, the other two being removed. In the first part of the experiment the observer was asked to match the intensity of the white field with that of the primary test field by flicker. During this measurement only the half of the field filled by both the primary and the white was visible. The speed of the sector was controlled by the observer so as to give the most accurate setting; five settings were usually taken. In the second part of the experiment both halves of the field were exposed, and the sector was run fast to remove flicker. The intensity of the primary was then set so that there was the smallest detectable difference in colour between the two fields, the intensities being kept equal throughout by means of the auxiliary wedge. In this way the intensities of the white and of the monochromatic radiation in the colour one step from the white could be found. This procedure was repeated at various points in the spectrum, and a curve showing the variation of the saturation-discrimination limen throughout the spectrum was drawn.

(5) For the measurement of the C.I.E. 1931 Standard Illuminant B a plane brass sheet covered with magnesium oxide was placed between the prisms *D* and *P*, with its plane normal to the direction of the light and so as to cut off the test colour beam. This surface was illuminated by the light from an N.P.L. standard lamp, the standard liquid filter being placed between the lamp and the surface.

§ 6. DISCUSSION OF RESULTS.

The results for all the observers are shown in figures 3 to 42. The characteristics of these curves will now be discussed, and the results for each observer compared.

The position of the observers on the Nagel distribution curve is shown in table 3, and compared with the normal mean and variation. It is immediately obvious that the position on the Nagel distribution curve cannot be taken as a measure of the defect of an observer as can his hue-discrimination curve, figures 4, 6, etc.

Table 3

Observer	$\log (R/G)$
Normal, mean	0.000
extreme on the deuteranomalous side	-0.170
extreme on the protanomalous side	0.170
Deuteranomalous, A	-0.695
B	-0.705
C	-0.560
D	-0.580
E	-0.425
F	-0.430
G	-0.860
Protanomalous, L	0.615
M	0.295

To some extent, however, it must be borne in mind that the readings given by the anomalous observers on the Nagel anomaloscope, except possibly those for observers A and D, cannot be compared in accuracy with those given on the colorimeter, where several readings could be taken and the observer was more at ease.

From the first glance it can be seen that the curves are different in type for each observer, and no attempt to take a mean as representative of the deuteranomalous observer could possibly be made. While this may also be true for the protanomalous observers, it is impossible to make the assertion from the complete results of only one observer (observer L).

While, in relating the characteristics of any observer, the hue-discrimination and spectral-mixture curves would have a definite connexion, this connexion is not of a simple character, as has been shown by the work of von Helmholtz⁽⁹⁾ and Schrödinger⁽¹⁰⁾ and in the search for an empirical relation by Judd⁽⁸⁾. It is therefore more convenient to discuss the curves for the hue-discrimination and the spectral coefficients together. The curves for observers A to F are shown together, as these are all deuteranomalous. These fall naturally into two groups, of which A, D, and F form one, and B, C, and E the other. In the case of the observer F only the spectral coefficients are shown. Both the spectral coefficients and the hue-discrimination curves of observers A and D are very similar in general shape to the normal. The points of minimum discrimination are in both cases moved towards the red, and the power of discrimination in the yellow is smaller than in the case of the normal.

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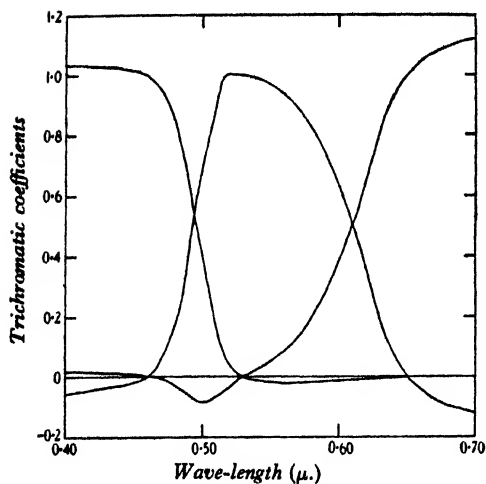


Figure 3. Spectral coefficients. J. H. N. (1) units. Observer A.

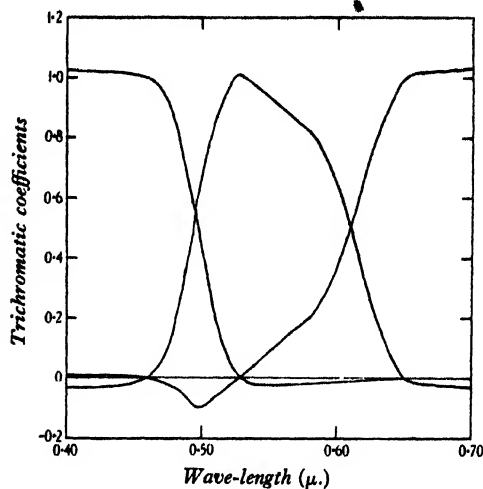


Figure 5. Spectral coefficients. J. H. N. (1) units. Observer D.

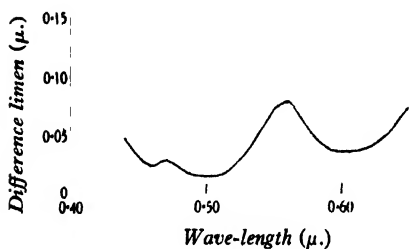


Figure 4. Hue-discrimination curve. Observer A.

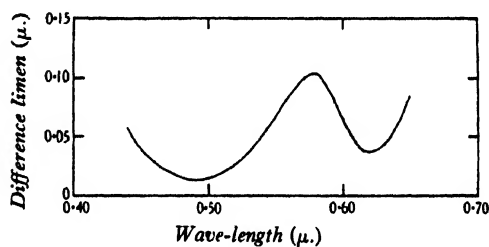


Figure 6. Hue-discrimination curve. Observer D.

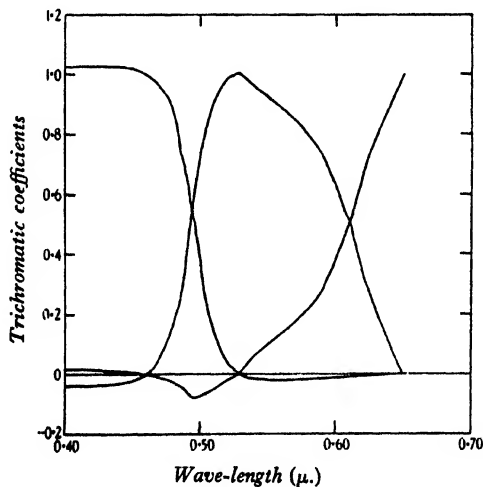


Figure 7. Spectral coefficients. J. H. N. (1) units. Observer F.

Observer A has a definite dip in the violet region, but this dip is absent in the case of observer D. The general shape of the spectral coefficients for observer F is also similar to that of the normal, although the coefficients change somewhat more sharply at about 0.54μ .

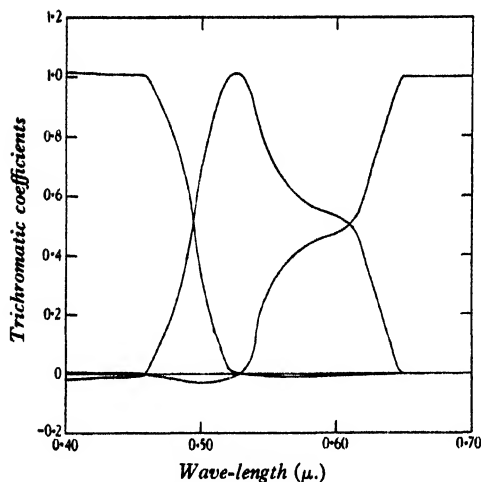


Figure 8. Spectral coefficients. J. H. N. (1) units. Observer B.

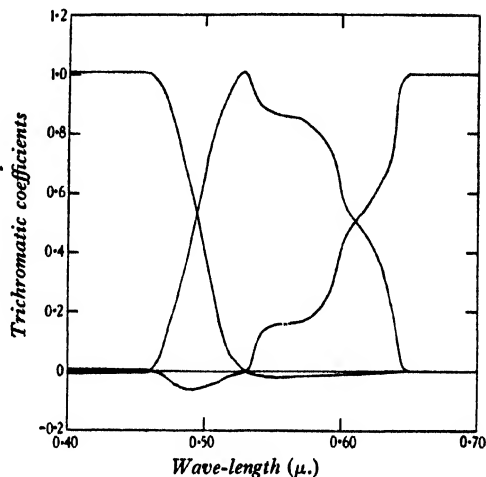


Figure 10. Spectral coefficients. J. H. N. (1) units. Observer C.

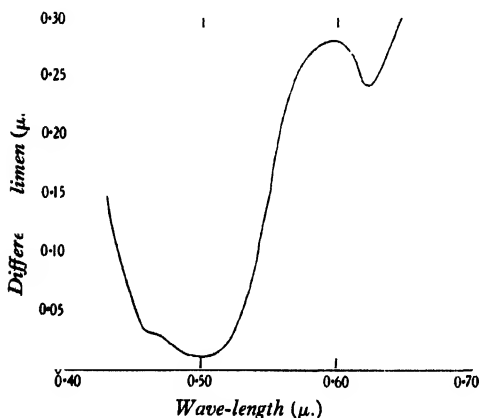


Figure 9. Hue-discrimination curve. Observer B.

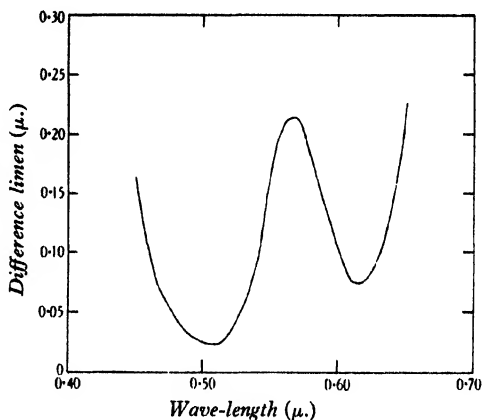


Figure 11. Hue-discrimination curve. Observer C.

In the case of all three of these observers, the negative blue coefficient in the yellow region and the negative red in the blue region were both necessary and readily measurable. Similarly in the violet and the extreme red regions the coefficients were readily obtainable.

It will be noticed that in the region of wave-length about 0.54μ , the coefficients in the curves for observers D and F change somewhat more sharply than those for the normal and for observer A, the effect being to move the rather flat portion of the coefficient curves towards the red. It is the accentuation of this effect which

differentiates the curves of observers B, C and E from those of observers A, D and F. It will be seen that with the presence of this flattening effect there is also a sharp rise in the value of the hue-discrimination limen. As far as the yellow region is concerned, observers C and E are somewhat similar, the difference limen has become large, and the point of minimum discrimination rather sharp. Observer B has even

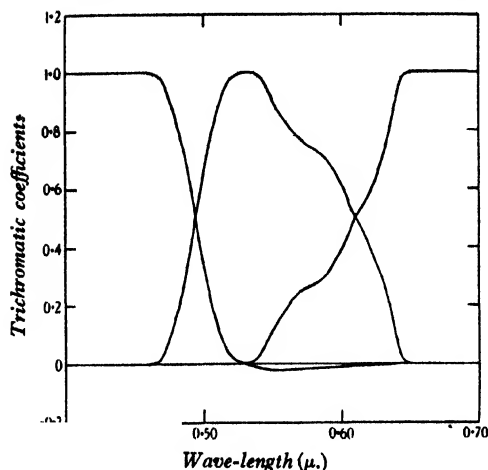


Figure 12. Spectral coefficients. J. H. N. (1) units. Observer E.

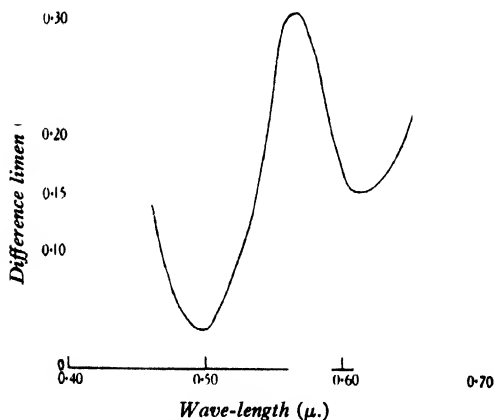


Figure 13. Hue-discrimination curve. Observer E.

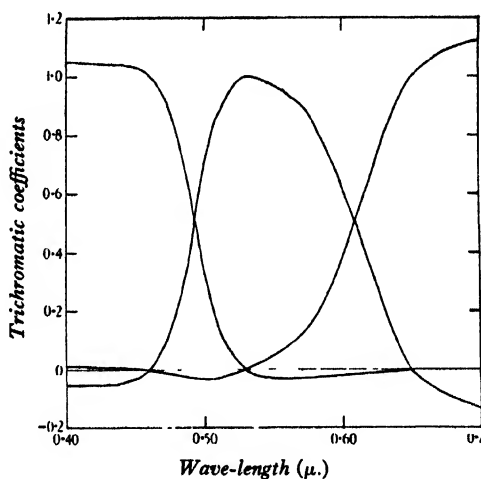


Figure 14. Spectral coefficients. J. H. N. (1) units. Normal observer.

poorer discrimination, and the flattening of the coefficient curves and the point of minimum discrimination are moved farther towards the red. At the same time in the blue-green region observer B has a very small difference limen, comparable with those of observers A and D. It shows a semblance of a dip in the violet, while the limen for observers C and E is considerably larger.

The existence of the negative blue coefficient in the yellow region is somewhat doubtful in all three cases, but the measurements tended to confirm its presence.

Although somewhat uncertain in value, it was, with the negative red in the blue-green region, definitely necessary in order to obtain a match in the case of observers B and C, but a match was obtained in the blue-green region by observer E with only the blue and green primaries. In all three cases it was found possible to obtain a perfect match between 0.70μ . and the red primary, and so no coefficients were measured in the extreme red. This would be expected also from the values of the hue-discrimination limen. In the violet in the case of observers B and C some difficulty was found in matching 0.43μ . with the blue primary, and it was not possible to match 0.41μ . In both these cases the red and green primaries were necessary for a satisfactory match, but the results were by no means certain or consistent. With observer E a perfect colour-match was obtained at 0.41μ . with the blue primary alone.

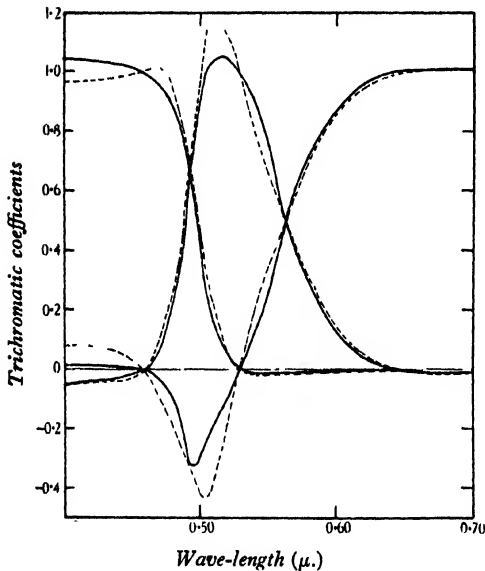


Figure 15. Spectral coefficients. J. H. N. (2) units. Observer L —; normal observer ----.

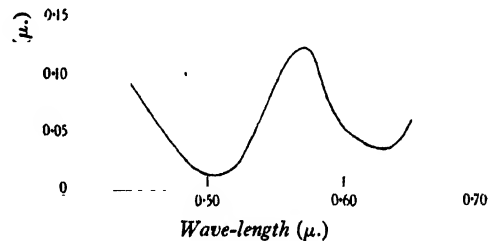


Figure 16. Hue-discrimination curve. Observer L.

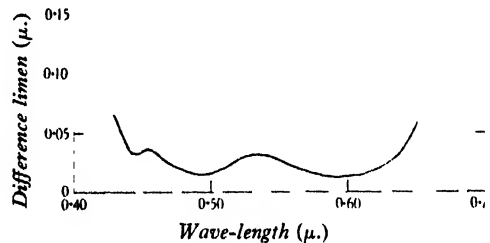


Figure 17. Hue-discrimination curve. Normal observer.

In the case of the above observers the coefficients can be compared with those of the normal observer expressed on the same system of units, J. H. N. (1), and the increased value of the red coefficient in the blue-green regions should be noticed. This increase was not present in the case of observer B but, while the negative red was necessary, an accurate setting could not be obtained in the region.

As the results for only one protanomalous observer are given, it is impossible to talk of any stages of protanomaly except by comparison with the results for the deuteranomalous observers. The spectral coefficients for observer L are expressed in a different set of units, J. H. N. (2), from those for the deuteranomalous observers, and they may be compared with the coefficients of the normal observer expressed in the same units. In the yellow region both curves are of the same type, while at the same time the hue-discrimination is nowhere very poor, being comparable with

that of observer D of the deuteranomalous observers. The angle of the red and green curves in the region of 0.54μ . is not as sharp as in the case of the normal, but this is to be expected in view of the difference in the values of the negative red coefficient in the blue-green region, and there cannot be said to be any flattening of the curves like that which was present in the case of the deuteranomalous observers. However, it must be noticed that the rate of change of slope in the case of the normal curve is continuous from about 0.52μ . to the extreme red, while this does not obtain in the case of observer L, his curve being convex between the extreme red and 0.56μ . and concave between 0.56 and 0.52μ . In the blue-green and violet regions the value of the red coefficient is less than the normal. In the former the negative red was necessary for the match and was readily measurable.

The hue-discrimination curve shows no secondary minimum in the violet region, and the discrimination extends farther into the extreme red than the normal, the value at 0.65μ . being little poorer than the normal and the slope of the curve somewhat less.

When the equal-energy luminosity curves of the deuteranomalous observers are compared with that of the normal observer, the differences are not so striking as in the case of other characteristics. Even the position of the maximum, by which the observer is conventionally defined; does not show a displacement towards the red greater than those which occur in the variation among normal observers. In the case of the one protanomalous observer the maximum of the luminosity curve is definitely moved to the blue, and lies between the normal maximum and the position of the maximum found by Pitt for protanopes, the red luminosity being depressed.

With regard to the definition of the protanomalous and deuteranomalous observers by means of their luminosity curves, it would be more satisfactory to define the protanomalous as having a relatively low red luminosity, compared with the normal, while the deuteranomalous should be said to differ but slightly from the normal, giving relatively more importance to the red than the green.

In the case of the spectral-mixture curves, the differences between the normal and the anomalous become even more marked than in the coefficient curves. Again we find the curves of observers A, D and F very similar. A similarity of shape would of course be expected, since the mixture curves are derived from the coefficient curves and the luminosity curve with a knowledge of the relative luminosity of the primaries. The similarity of the mixture curves therefore implies that both the coefficients and the relative luminosities of the primaries are similar. The red curve is depressed nearly uniformly in comparison with the normal, while the green curve fills out in proportion. In the blue and violet regions the blue curve is depressed, and the red and green curves are nearer the axis, while the total luminosity is of the same order as the normal. The luminosity curve for observer D is broader than the normal, and there is a small irregularity in the red curve.

The curves for observers C and E are again very similar, but the differences between them and those for observer B have become more marked. The irregularity in the red curve is quite marked, but the total luminosity curve for observer E has a

rather broader maximum than the normal and in consequence the green curves differ. In the case of observer B the red and green curves tend to run almost parallel over a long range, hence the red luminosity is increased relative to the green, and the curve falls very sharply just before 0.53μ . The blue curves are still further

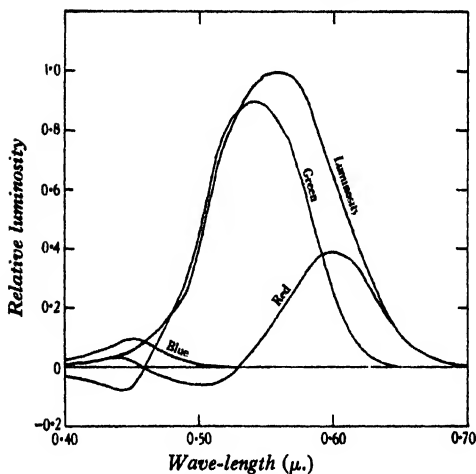


Figure 18. Luminosity and mixture curves for equal-energy spectrum. Normal trichromat.

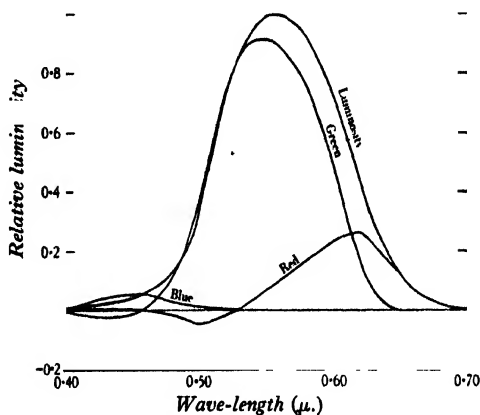


Figure 20. Luminosity and mixture curves for equal-energy spectrum. Observer D.

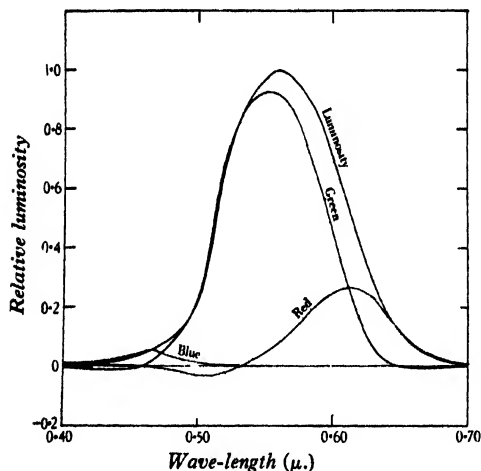


Figure 19. Luminosity and mixture curves for equal-energy spectrum. Observer A.

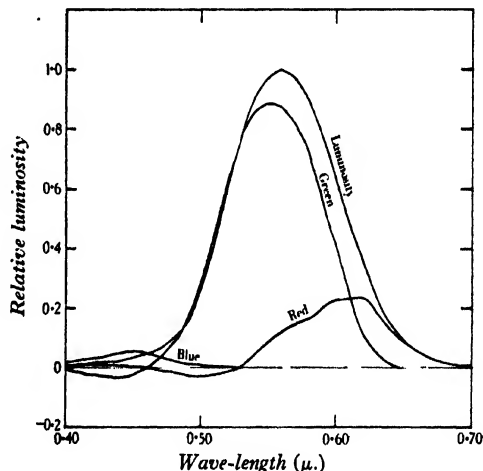


Figure 21. Luminosity and mixture curves for equal-energy spectrum. Observer F.

depressed in all three cases, reaching a little more than one-fifth of the normal value for observer B. At the same time the red and green luminosities have become negligible in this region.

In consequence of the reduction of the total luminosity of the red region of the curve for observer L, the red mixture curve becomes very small, being comparable with the blue curve. Throughout the central region the green curve dominates the

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mixture, but in the violet region the negative green is small and the red is negligible, the mixture being dominated by the blue. In this region the blue luminosity is of the same order as the normal; thus since the red and green are less important, the blue is relatively more important for the protanomalous than for the normal ob-

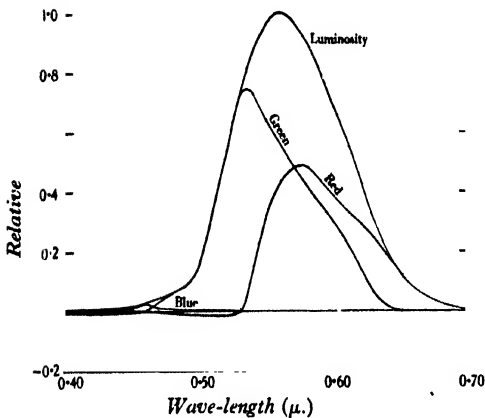


Figure 22. Luminosity and mixture curves for equal-energy spectrum. Observer B.

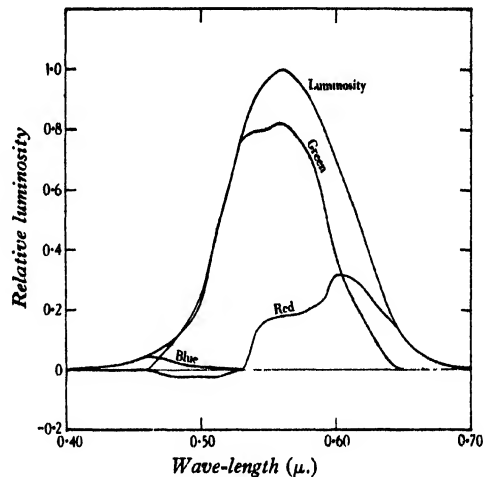


Figure 23. Luminosity and mixture curves for equal-energy spectrum. Observer C.

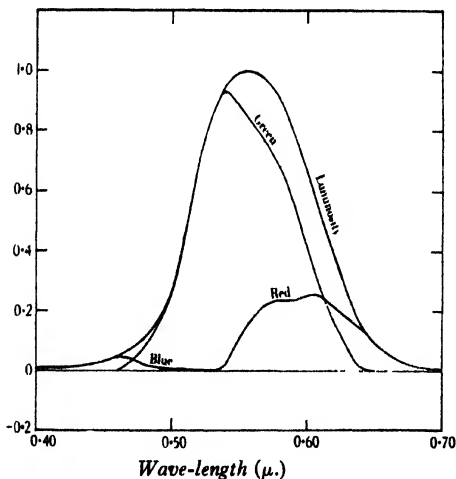


Figure 24. Luminosity and mixture curves for equal-energy spectrum. Observer E.

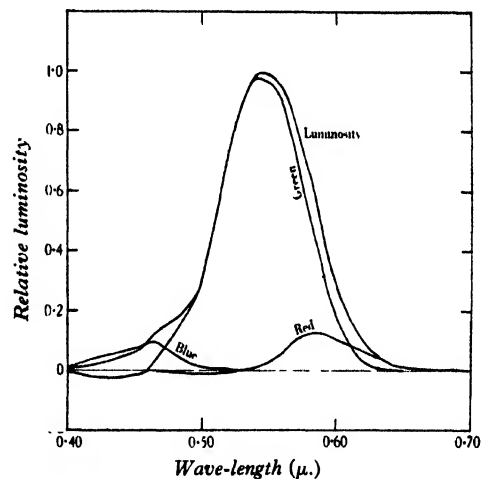


Figure 25. Luminosity and mixture curves for equal-energy spectrum. Observer L.

server. It is interesting to note that in spite of this blue dominance and consequent smallness of the change in relative composition with wave-length, the hue-discrimination is not made very much poorer than the normal.

Saturation-discrimination curves have only been taken for observers B, D and E. We have seen that in the red-yellow-green region the hue-discrimination is low and in consequence the colours are all much more similar than in the case of the normal

observer. Since the colours are very similar it is natural that the differences between them and white should be more nearly the same; thus it is to be expected that the saturation-discrimination will not change much with wave-length in this region. This is found in practice with all three observers, the value of the saturation-discrimination corresponding approximately to the lowest value for the normal; thus the colours appear very desaturated. In the blue-green region the curve rises sharply, in the case of observer B to the same order of value as the normal, though in the case of observers D and E the rise is not so sharp. Again both the sharp rise in

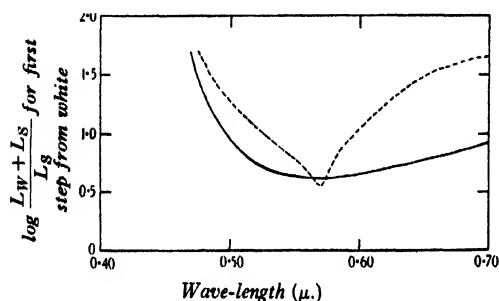


Figure 26. Curves for saturation-discrimination. Observer B. Dotted curve gives normal values for comparison.

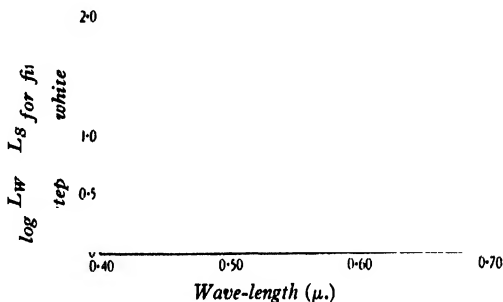


Figure 27. Curve for saturation-discrimination. Observer D.

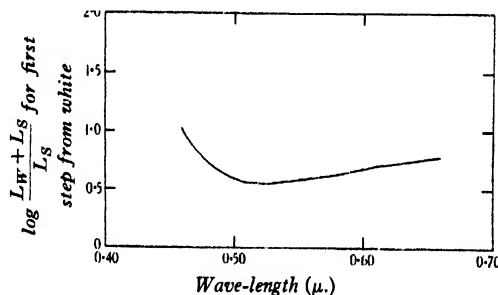


Figure 28. Curve for saturation-discrimination. Observer E.

the curve for observer B and the slower rises for observers D and E compare favourably with what would be expected from the respective hue-discrimination curves, that of observer B being of the same order as the normal in the blue-green region.

The trichromatic coefficients have also been shown in the form of a colour-triangle. While the shape of the triangle will depend mainly on the choice of unit colours, the differences between the observers are readily shown by the differences in the grouping of the points for different wave-lengths and by the position of the white (S_B) point. The position of this white point may be compared with that of the normal observer shown in the same system. The difference between the normal and the anomalous position of the white point falls, for the observers shown, into roughly two classes. In the case of observers A, B, C and E it is displaced towards

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the yellow and the yellow-green, but in the case of observers D and F it is displaced predominantly towards the red.

The colour-triangles have been used to find the complementary wave-lengths for each observer. With the exception of the curve for observer C these are of the

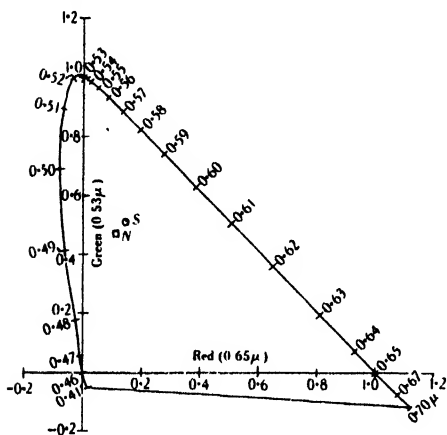


Figure 29. Spectral locus plotted in colour-triangle. J.H.N. (1) units. Observer A. N, white point for normal observer; S, white point for observer A.

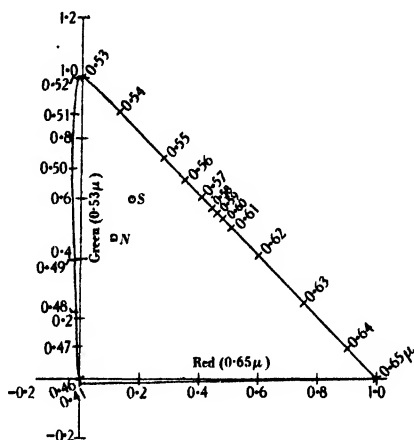


Figure 30. Spectral locus plotted in colour-triangle. J.H.N. (1) units. Observer B. N, white point for normal observer; S, white point for observer B.

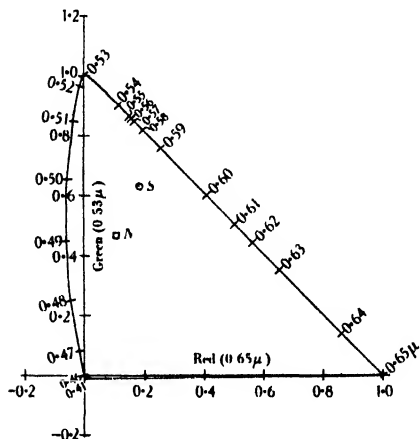


Figure 31. Spectral locus plotted in colour-triangle. J.H.N. (1) units. Observer C. N, white point for normal observer; S, white point for observer C.

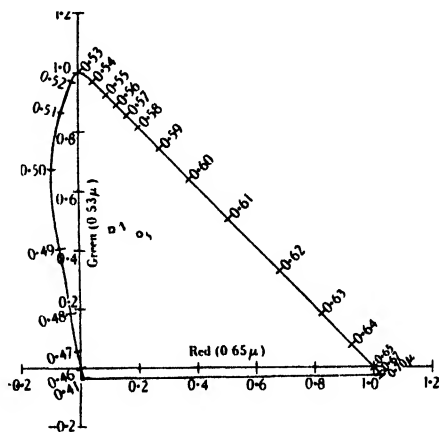


Figure 32. Spectral locus plotted in colour-triangle. J.H.N. (1) units. Observer D. N, white point for normal observer; S, white point for observer D.

same smooth type as for the normal, the curve for observer C being re-entrant at about 0.61μ . At the red end of the spectrum all the curves are of the same order as the normal, but there are considerable differences in the violet end, observers A, C, D and F requiring a wave-length between 0.58 and 0.60μ . to mix with 0.40μ , while observers B and E require between 0.54 and 0.56μ , the normal value being about 0.57μ . In the case of observer L there is a change in the red, the wave-length

to be mixed with the extreme red being changed from about 0.50μ . for the normal to about 0.49μ . The change in the violet is of the same order, being from about 0.57 to 0.58μ .

In the above discussion of results, it has been possible in the discussion of each particular characteristic to divide the observers into classes which are more or less

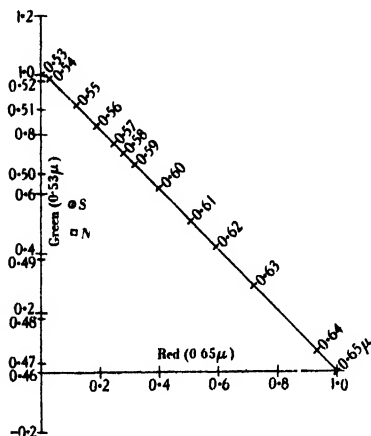


Figure 33. Spectral locus plotted in colour-triangle. J. H. N. (1) units. Observer E. N, white point for normal observer; S, white point for observer E.

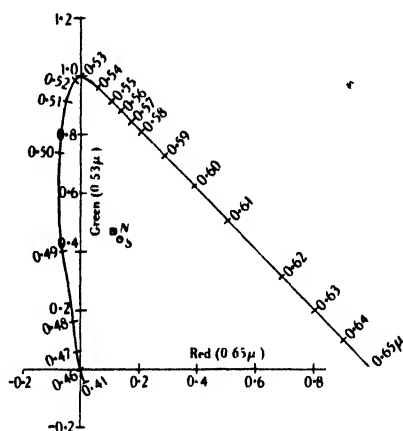


Figure 34. Spectral locus plotted in colour-triangle. J. H. N. (1) units. Observer F. N, white point for normal observer; S, white point for observer F.

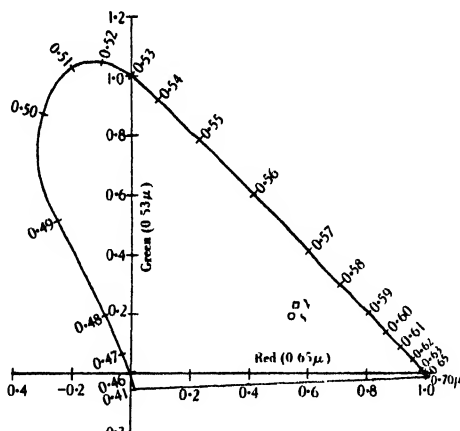


Figure 35. Spectral locus plotted in colour-triangle. J. H. N. (2) units. Observer L. N, white point for normal observer; S, white point for observer L.

similar. It is of interest to express these classes in a table; this has been arranged so that the members of group I are in general more similar to the normal than those of group II (table 4).

In addition to the results obtained for observers A to F and L, observations were made by several other observers. Observer G (figure 43) is a deuteranomalous observer with approximately the same amount of defect as observer C, according to

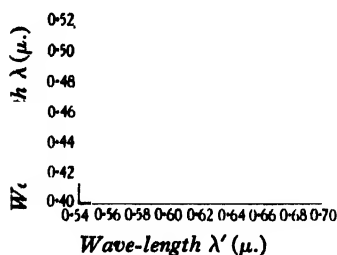


Figure 36. Relation between complementary wave-lengths λ and λ' , for observer A.

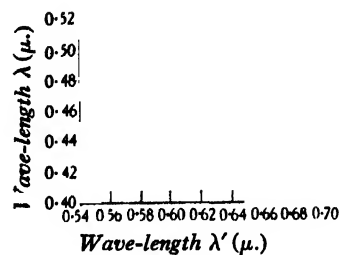


Figure 37. Relation between complementary wave-lengths λ and λ' , for observer B.

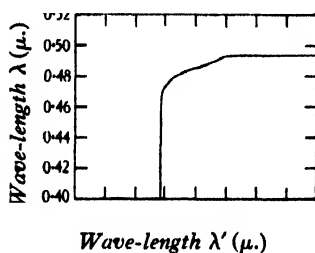


Figure 38. Relation between complementary wave-lengths λ and λ' , for observer C.

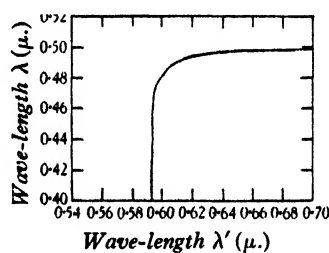


Figure 39. Relation between complementary wave-lengths λ and λ' , for observer D.

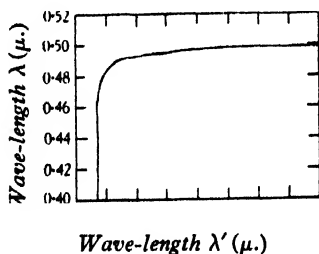


Figure 40. Relation between complementary wave-lengths λ and λ' , for observer E.

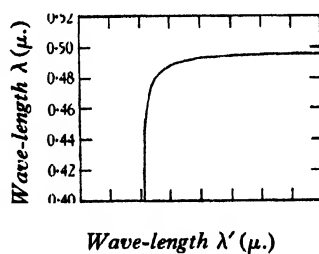


Figure 41. Relation between complementary wave-lengths λ and λ' , for observer F.

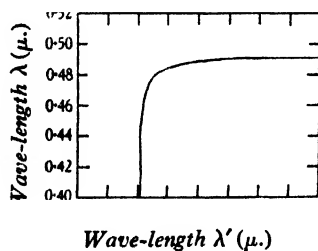


Figure 42. Relation between complementary wave-lengths λ and λ' , for observer L.

the hue-discrimination curve shown. This curve is especially interesting, however, as it is probably by far the most accurate of the curves showing very poor discrimination, since the observer was very careful in making his observations. At this point it is convenient to point out that curves showing very poor discrimination and very rapid changes in the value of the difference limen cannot be obtained with any high degree of accuracy. Suppose, for example, that the observer G is taking a step towards the red, which in reality ends at 0.56μ .; now at 0.56μ . the limen is rising rapidly, and thus the change in colour is small and becoming smaller, and therefore it is very easy to pass to a place beyond the maximum, say at 0.60μ ., where the

Table 4

Characteristic	Group I	Group II	Group III
Trichromatic coefficients	A, D, F	B, C, E	B
Hue-discrimination	A, D	B, C, E	
Mixture curves	A, D, F	C, E	
Saturation disc	B	D, E	
Colour-triangle	A, C	B, D, E, F	C
Complementary wave-lengths	A, D, F	B, E	

limen is decreasing and thus the step is more easily determined. As can be seen this would add 0.04μ . to the value of the step. It is possible to ensure against this type of error to a certain extent by repetition of the results, when those which are not consistent must not be included; the safest method is, however, for the observer to take extreme care in making the step, and to make the step in such a way that he never sees more than the minimum difference; for instance, in the above example, the whole of the step must be made in the direction from the green to 0.56μ . This method was used as far as possible in making observations in such parts of the curve, but it is very tedious and requires the observer to have great patience.

The curve shown for observer H is incomplete, as the readings in the violet have only been taken roughly. Although that part of the curve is not shown, there is a secondary minimum, as seems usual with the normal trichromat. The observer was to all intents normal, the rise in the yellow region being only from the normal value of 0.0010 to 0.0015μ .; his position on the Nagel distribution curve was, however, on the extreme of the normal towards the deuteranomalous.

Observations were taken by two further protanomalous observers. A large number of results were taken by the first, who found colour-matching rather difficult in that he could not give constant readings for the proportion of the red-green and blue constituents, and could do so still less for the luminosity values. Before the observations were discontinued, attempts were made to obtain hue-discrimination readings; these also were very inconsistent. In the case of the second observer, M, it was found possible to obtain a hue-discrimination curve. The curve shows a high discrimination in the violet, but no secondary minimum. In the case of the coefficients the values of the proportions of the constituents were quite constant, but the luminosity values varied widely, two consecutive readings differing by as much as 100 per cent. Several attempts were made to obtain

accurate settings before the readings were discontinued. It seems worth recording that such an effect was not found in the case of any of the deuteranomalous observers, or in the case of observer L. Any difficulties found in the case of the deuteranomalous luminosity curves were generally definite errors, which appeared also in the values of the coefficients.

One observer was found and classed as deuteranomalous from his Nagel reading; this classification was borne out by his luminosity readings, but his hue-discrimina-

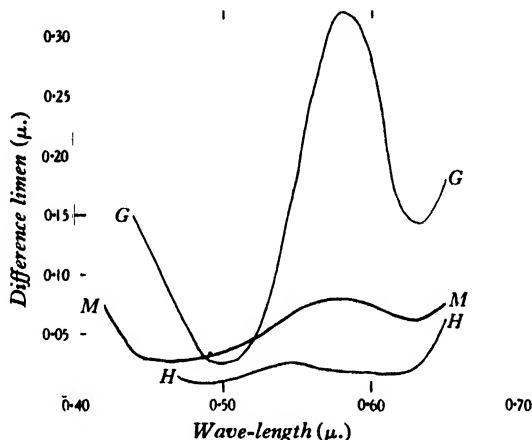


Figure 43. Hue-discrimination curves. Observers G, H, M.

tion showed only about two colour steps between 0.54 and $0.65 \mu.$, and it was impossible to obtain any coefficients in the yellow region. Measurements were then taken with the blue and green primaries alone, as if the observer had been a deuteranope, and in the region between 0.46 and $0.59 \mu.$ satisfactory matches were obtainable, but it was found impossible to obtain a match at $0.65 \mu.$ No results are given for this observer; the coefficients between 0.46 and $0.53 \mu.$ are similar to those given by Pitt for a deuteranope. Clearly in the case of the coefficients in the yellow region some special convention would have to be adopted, owing to the large tolerances by which a match must be defined for this type of observer.

§7. PREVIOUS INVESTIGATIONS

As regards the statistical survey, there have already been several very full sets of results for the percentage of colour anomalies occurring. Those of Schmidt⁽⁷⁾, Waaler⁽¹¹⁾ and von Planta⁽¹²⁾ have been referred to and comparison has been made. In his paper von Planta gives a survey of a large number of sets of statistics, and discusses the possibility of racial differences. However, while these workers used the anomaloscope, they do not publish a curve or table showing the variation of the red-to-green ratio needed in the match for different observers, although such a curve is given by Houston⁽¹⁸⁾. For the author's purpose a repetition of the results was in any case necessary, for it was desirable to know the position on the distribution curve of the anomalous observers examined, and if possible to select a wide

range of observers. In practice it was necessary to select the observers for their reliability rather than for their position on the distribution curve, although, as can be seen from table 3, the range also is satisfactory.

The results obtained by Schmidt, Waaler and von Planta show that a large number of women were examined; in the author's examination men were chosen in preference to women owing to the relatively greater chance of finding observers with defective colour-vision.

After the discovery of anomalous trichromatism by Lord Rayleigh⁽²⁾, many cases were investigated, notably by Hering⁽¹³⁾, von Kries⁽¹⁴⁾, and Abney and Watson⁽¹⁵⁾. The measurements taken by these workers were mainly concentrated on the luminosity values, which, as can be seen, do not vary as much as the other characteristics. The possibility of anomalous trichromatism being caused by a colour pigment is discussed by von Kries, and he shows that this explanation is unsatisfactory by comparing the ratio of red to green needed to match various colours in the yellow region for both normal and anomalous observers. Much of Abney's research on anomalous trichromatism seems to have been based on the assumption that the difference between normal and anomalous trichromatism was caused by a reduction or shift of one of the sensation curves.

In the main, in assessing the value of the results obtained by earlier investigators, it must be borne in mind that the intensity of light available was very low, and the question of stray light was not dealt with sufficiently; these points are if anything of more importance in the investigation of anomalous than of normal observers, since the tolerances for a match in the yellow region are often very large, and ease of observation will tend to reduce these tolerances to a minimum.

In the measurement of the hue-discrimination limen the necessity of equating the intensities of the two halves of the field throughout the observation was not realized until quite recently. In general the two halves were made equal in intensity when the wave-lengths were the same, and then one wave-length was changed until the smallest detectable difference between the two halves was found. Clearly, in view of the variation of luminosity with wave-length, the limen found by this method will be due to differences partly of colour and partly of intensity.

Steindler⁽¹⁶⁾ gives the hue-discrimination curves for normal trichromats and for dichromats, but the precaution of keeping the two halves of the field at the same intensity was not taken, and so the results are not comparable with other measurements. It is, however, worth noting that the curve given as for a protanope shows discrimination in the yellow region of the spectrum, and may therefore have been for a protanomalous observer. As, however, the limen in which the results are expressed is a complex mixture of intensity and colour, this is by no means certain.

The importance of eliminating stray light in hue-discrimination measurements cannot be over-estimated. For example, during a series of observations in the violet region for observer A the apparatus was found to be out of adjustment in such a way as to allow a small quantity of stray light to enter, and the results bore no relation to those obtained immediately after the apparatus had been readjusted.

The results obtained by Pitt were taken with the apparatus used by the author,

so that the necessary precautions as to stray light and the convenience of observation were those fully detailed by Wright in his paper describing the apparatus. Reference to Pitt's paper will show that luminosity, spectral-mixture, and hue-discrimination curves for three deuteranomalous observers W. F. T., E. H. B. M., D. H. K. L. are given. These observers can be seen to belong to the same type as the author's observers A and D; it is in this respect that the results obtained by the author differ from those obtained by Pitt, for although there are not many more observers they vary considerably in type. In the case of observers W. F. T. and D. H. K. L. the point of maximum luminosity has been moved to the red more than in the case of observers A and D, being at about 0.57μ . The curves for W. F. T. are somewhat different from the rest both of Pitt's and of the author's observers, the blue-mixture curve being more comparable with the normal in size, but having its maximum moved to the violet, while the red-mixture curve has its maximum moved to the red. This displacement is accompanied by an extension of the hue-discrimination curve into both the red and the violet regions far beyond the normal. A further point of interest is a comparison between the green-mixture curves of observers D. H. K. L., E and B, there being a general similarity of shape in the neighbourhood of 0.56μ . in all three cases, notwithstanding the fact that the characteristics as a whole are different.

§ 8. THEORETICAL CONSIDERATIONS

Since the anomalous trichromat has a trichromatic system of colour-vision, each match is unique, although in practice it may be difficult to determine the exact constituents of the match. Owing to the poor hue-discrimination in the yellow region it will be possible to select two colour mixtures, both of which match the same spectral colour for the anomalous trichromat. These same two mixtures would of course be different for the normal trichromat and may perhaps both fail to match the spectral colour. Such a state of affairs must not be considered to mean that the match for the anomalous trichromat is not unique, since it is merely caused by unusually large tolerances that this type of observer gives to a colour match. In applying the term "unique" to the anomalous match, or for that matter to the normal match, a range of mixtures, the size of which is determined by the hue-discrimination, must be considered as satisfying the match, but outside this range there is no other range that would do so. Further, it is necessary to consider that the hue-discrimination has a definite finite value in the region; for instance if a dichromat is asked to make a match in the yellow region using red, green, and blue primaries, then the settings for the red and green readings cannot be unique if the primaries are such that he can obtain a perfect colour-match between the red and green primaries.

The match given by the anomalous trichromat is not the same as that given by the normal trichromat, and conversely the normal match is not valid for the anomalous observer, as it is in the case of the dichromat. From the statement that the normal match is not valid for the anomalous observer, the limiting type of observer mentioned at the end of § 5 must be excepted, since for him the normal

match is satisfactory as a result of the large tolerances allowed for a match by this type of observer. The importance of the fact that the normal and anomalous matches are different and that the normal match is not satisfactory for the anomalous observer cannot be stressed too highly, and in any attempt to correlate normal and anomalous trichromatism it makes any uniform reduction of one of the hypothetical fundamental sensation curves invalid as an explanation⁽¹⁾.

An examination of the Nagel distribution curve is the most natural beginning in a discussion of the nature of the relation between normal and anomalous trichromatism. To the question whether the anomalous trichromats are an intermediate stage between normal trichromats and dichromats, the continuous form of the Nagel curve would suggest an affirmative answer. But if this question is modified and we wish to know whether there is a continuous gradation between normal and dichromatic vision, the curve gives a modified answer. On the protanomalous side of the curve we find a continuous gradation from the normal to the dichromat; owing to the fact that the number of observers examined was not very large, any small irregularities which might be present would not be evident, but if they exist they must be smaller than the maximum found for the deuteranomalous. On the other hand, on the side of the deuteranomalous observers we find a secondary maximum in the curve, showing that while there may be observers at any point between the normal and the deuteranope there is one place at which the formation of anomalous trichromatism is more likely than elsewhere.

Suppose we consider the evolutionary development suggested by McDougall⁽¹⁷⁾ on the basis of the trichromatic theory. According to this theory, from the monochromatic state the blue and yellow sensations are supposed to have developed first, and later the yellow is supposed to have split up into red and green. The type of curve to be expected from this theory would be a central maximum with the sides sloping away to the protanopes and the deuteranopes, and the rates of falling off would be in some way proportional to the numbers of protanopes and deuteranopes respectively. Alternatively, purely on the grounds of probability, the type of curve to be expected would have a sharp central maximum and fall away equally on each side. In practice, on the protanomalous side there is a uniform rate of falling away, but the number of observers found at a distance from the central maximum is perhaps greater than would be expected purely on the grounds of probability. On the side of the deuteranomalous observers, on the other hand, there is a secondary maximum reaching a height of about $1/25$ of the main maximum, and being much flatter it spreads over about the same range on a logarithmic scale as the main maximum. The existence of this maximum shows that in some way the deuteranomalous state is peculiar and is to be distinguished from other forms of colour deficiency. From the point of view of evolutionary development, the existence of so many deuteranomalous observers and their particular distribution would indicate that the state was evolutionarily stable as compared with the protanomalous state. This might be taken to mean that in the splitting of the yellow sensation, as visualized by McDougall, two stages are necessary for the complete process in the transition between the deuteranope and the normal. Alternatively in view of the

fact that Schmidt⁽⁷⁾ finds a definite gap between the normal and deuteranomalous observers in the Nagel distribution curve, it may be that there are two alternative ways in which the deuteranopic state may develop, the most usual being a development to the normal, and the secondary being a development to the deuteranomalous state. While the latter arrangement should be considered as possible, it would seem to be unlikely since it would imply that there were two distinct forms of deuteranope and that, further, in the most usual change (between the deuteranope and the normal) there were no intermediate stages as there are in the case of the protanomalous observers, although the existence of observers throughout the whole range in the case of the author's results would supply this deficiency. Further, the symmetrical shape of the deuteranomalous maximum would seem to support the idea of a continuous transition between the deuteranope and the normal, with a preferential state corresponding to the deuteranomalous maximum.

Before considering the mechanism by which these changes may be produced, it is convenient to discuss the characteristics of the anomalous trichromats in a general way and to compare them with those of the normal trichromat. The general form of the curves for the anomalous trichromat is similar to that for the normal trichromat, but in the hue-discrimination curves we find a definite shift of the salient points towards the red end of the spectrum for both protanomalous and deuteranomalous observers. Moreover this shift is not limited to the yellow region, but in the case of observers A and B, where there is a point of maximum discrimination in the violet region, this is also moved towards the red. In the case of two of Pitt's observers this shift towards the red only holds in the yellow region, the blue-green point of maximum discrimination being moved towards the violet.

In an appendix to Pitt's report on dichromatism⁽¹⁾, W. D. Wright gives a theoretical discussion, and points out that if an observer is asked to point to the colour in the spectrum between red and green, which has the properties of neither red nor green, then most observers will point to very nearly the same place.

During the investigations each of the anomalous observers was asked to point to this "pure yellow," and when a ground glass screen was placed in the spectrum it was found that the observers were very definite about the position of the yellow, which was slightly to the green side of the normal in the case of the protanomalous and to the red in the case of the deuteranomalous. When the observers were asked to set the test colour of the colorimeter, however, it was not generally possible to get concordant results. The results for observer C were sufficiently good to enable a mean to be taken, and a value of 0.595μ . was found, as compared with approximately 0.580μ . for the normal. In the movement of the colour which the observer calls "pure yellow", we find a movement one way for the protanomalous and the other way for the deuteranomalous, while in the characteristic points of the hue-discrimination curve both protanomalous and deuteranomalous are moved in the same direction.

If the differences between the normal and anomalous hue-discrimination curves are taken as a measure of the degree of deficiency of the observer, then it can be seen

that the other characteristics cannot always be treated as an obvious guide to the extent of the defect. The mixture curves should to some extent be excepted from this, as in a general way they show the sensitivity of the observer to changes in hue. In the case of the protanomalous observer the evidence of his relatively high hue-discrimination in the red would not seem to be present; however it is at the ends of the spectrum that the difference between theory and practice becomes most evident in the theoretical curves given by von Helmholtz⁽⁹⁾ and Schrödinger. If a relation is

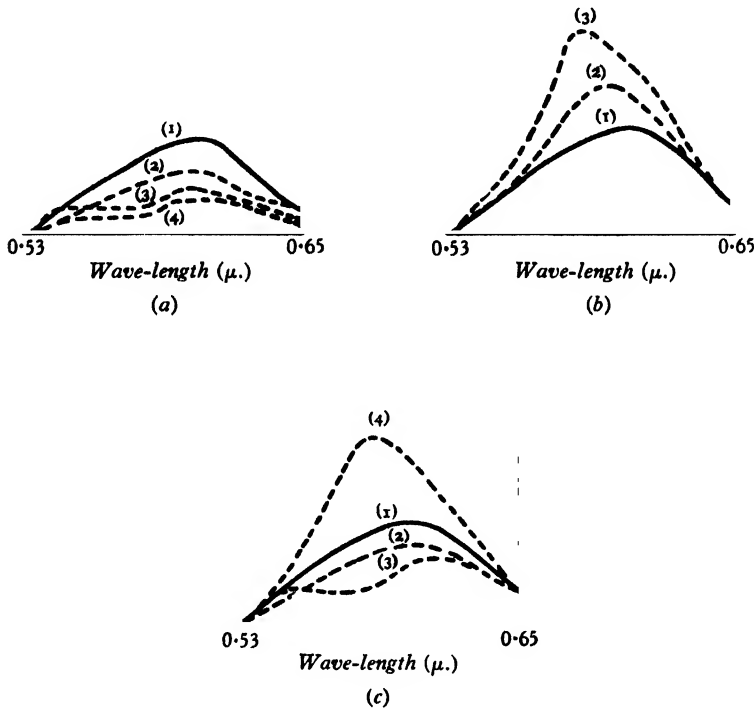


Figure 44. Showing the possible changes in the red luminosity curve between the normal and the dichromat.

found between the difference limen and the differential coefficients of the proportions of the fundamental sensations with respect to the wave-length, or, more generally, between the difference limen and some function of the fundamental sensations, it must apply equally to all forms of colour-vision. In fact the true relation would only require that the appropriate fundamental sensations should be used, when it would be equally applicable to the normal, the anomalous trichromat, and the dichromat. In fact the most thorough test of such a relation, when it has been worked out for a normal trichromat, would be its application to the characteristics of an anomalous trichromat. This apparent discrepancy between the various characteristics is particularly noticeable as regards the position on the Nagel distribution curve. For example in the case of observers A and D (see tables 3 and 4)

A is farther from the normal than D on the Nagel curve, but his hue-discrimination is the more nearly normal. To some extent this can be accounted for by the differences in relative luminosity, as can be seen by a comparison of the luminosity curves in the regions of 0.535 and 0.65 μ . Thus the individual characteristics cannot be regarded as a continuous series of states between normal trichromatism and dichromatism.

The changes between normal and anomalous observers shown in the mixture curves appear to be of a complex nature. The problem is complicated by the form of the red curve in the cases of observers C and E. From the point of view of the mixture curves, there seem to be three possible ways through which a series of changes between normal and dichromat could be made. These can be best shown by means of figures; in figures (44*a*) and (44*b*) we have the changes shown as two entirely separate mechanisms, which must both exist together. In (*a*) the change is obtained by a transformation from the normal through the types represented by observers C and E and the final disappearance of the red curve into insignificance. In the case of method (*b*) the changes are given an alternative path passing from the normal to the type represented by observer B, the red curve finally merging into the green curve. The third possibility is in reality a combination of the former two, and is shown in figure (44*c*). In this case the changes are supposed to take place, from the normal, through the types represented by observers A and C and finally instead of the red curve disappearing, the point of inflection is moved higher up the curve, giving the type represented by observer B, and the red curve joins up with the green curve as in case (*b*).

The idea of there being two evolutionary modes in the case of the deuteranomalous was introduced previously (page 687) and in this case the possibility of the deuteranomalous as an alternative final state was suggested. This might be modified to include two types of change, the first, similar to the protanomalous, being continuous between normal and deuteranope, and the second series having a preferential state through which it must pass or at which it must remain, corresponding to the maximum in the deuteranomalous region.

The actual mechanism by which such changes may be produced are clearly complex, and will probably not rest entirely in the photochemical changes or in the subsequent analysis. While the possibility of some differences between the photochemical substance in the retina of the normal and anomalous observers might be considered, further evidence from adaptation phenomena and the physiology of the anomalous eye is necessary.

§9. ACKNOWLEDGEMENTS

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Table 5. Characteristics for observer A

Wave-length λ (μ)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients J. H. N. (1) units			Mixture curves for equal-energy spectrum			Complementary wave-lengths (μ)		Hue-dis-crimina-tion; just-noticeable wave-length dif-ferences (μ)	Satura-tion-dis-crimina-tion log $\frac{L_W + L_S}{L_S}$	Wave-length λ (μ)
		B (0.46 μ)	G (0.53 μ)	R (0.65 μ)	L _B	L _G	L _R	λ	λ'			
0.41	0.0060	1.032	-0.050	0.018	0.0096	-0.0055	0.0019	0.41	0.5820	—	—	0.41
0.43	0.0120	1.024	-0.037	0.013	0.0167	-0.0071	0.0024	0.43	0.5825	0.0048 (0.44)	—	0.43
0.45	0.0286	1.016	-0.021	0.005	0.0351	-0.0085	0.002	0.45	0.5836	0.0033	—	0.45
0.46	0.050	1.000	0.000	0.000	0.050	0.000	0.000	0.46	0.5842	0.0025	—	0.46
0.47	0.073	0.951	0.057	-0.008	0.045	0.032	-0.004	0.47	0.5858	0.0029	—	0.47
0.48	0.100	0.849	0.178	-0.027	0.032	0.080	-0.012	0.48	0.5888	0.0023	—	0.48
0.49	0.140	0.651	0.410	-0.061	0.019	0.141	-0.020	0.49	0.5997	0.0017	—	0.49
0.50	0.234	0.393	0.690	-0.083	0.008	0.251	-0.029	—	—	0.0016	—	0.50
0.51	0.438	0.171	0.896	-0.067	0.008	0.463	-0.033	—	—	0.0017	—	0.51
0.52	0.683	0.033	1.001	-0.034	0.002	0.704	-0.023	—	—	0.0024	—	0.52
0.53	0.828	0.000	1.000	0.000	0.000	0.828	0.000	—	—	0.0036	—	0.53
0.54	0.919	-0.015	0.992	0.023	0.000	0.899	0.020	—	—	0.0054	—	0.54
0.55	0.974	-0.020	0.970	0.050	0.000	0.929	0.045	—	—	0.0072	—	0.55
0.56	1.000	-0.022	0.934	0.086	0.000	0.918	0.082	—	—	0.0079	—	0.56
0.57	0.976	-0.020	0.886	0.134	0.000	0.853	0.123	—	—	0.0065	—	0.57
0.58	0.918	-0.018	0.821	0.197	0.000	0.743	0.175	—	—	0.0048	—	0.58
0.59	0.830	-0.015	0.740	0.275	0.000	0.612	0.218	0.4811	0.59	0.0039	—	0.59
0.60	0.692	-0.012	0.627	0.385	0.000	0.435	0.251	0.4902	0.60	0.0036	—	0.60
0.61	0.547	-0.010	0.505	0.505	0.000	0.279	0.268	0.4936	0.61	0.0037	—	0.61
0.62	0.408	-0.008	0.360	0.648	0.000	0.150	0.258	0.4957	0.62	0.0040	—	0.62
0.63	0.289	-0.005	0.195	0.810	0.000	0.058	0.231	0.4973	0.63	0.0046	—	0.63
0.64	0.183	-0.003	0.072	0.931	0.000	0.014	0.169	0.4981	0.64	0.0058	—	0.64
0.65	0.110	0.000	0.000	1.000	0.000	0.000	0.110	0.4984	0.65	0.0073	—	0.65
0.67	0.0316	0.000	-0.077	1.077	0.000	-0.0025	0.0341	—	—	—	—	0.67
0.70	0.0056	0.000	-0.120	1.120	0.000	-0.0007	0.0663	0.4989	0.70	—	—	0.70
1931 C.I.E. S_B source		0.343	0.511	0.146	Relative luminosities of trichromatic units of primaries							
$\lambda = 0.61 \mu$		-0.010	0.505	0.595	0.46 μ	0.53 μ	0.65 μ					
$\lambda = 0.5825 \mu$		-0.017	0.803	0.214	0.085	1.000	0.959					
$\lambda = 0.4940 \mu$		0.537	0.537	-0.074								

Table 6. Character for obse: B

Wave-length λ (μ .)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients J. H. N. (1) units			Mixture curves for equal-energy spectrum			Complementary wave-lengths (μ .)		Hue-dis-crimina-tion; just-noticeable wave-length dif-ferences (μ .)	Satura-tion-dis-crimina-tion log $\frac{L_W + L_G}{L_B}$	Wave-length λ (μ .)
		B (0.46 μ .)	G (0.53 μ .)	R (0.65 μ .)	L_B	L_G	L_R	λ	λ'			
0.41	0.005	1.014	-0.019	0.005	0.0070	-0.0033	0.0013	0.41	0.5453	—	—	0.41
0.43	0.010	1.010	-0.013	0.003	0.0128	-0.0042	0.0014	0.43	0.5454	0.0146	—	0.43
0.45	0.012	1.008	-0.009	0.001	0.0148	-0.0034	0.0006	0.45	0.5456	0.0052	—	0.45
0.46	0.023	1.000	0.000	0.000	0.023	0.000	0.000	0.46	0.5457	0.0032	—	0.46
0.47	0.040	0.907	0.105	-0.018	0.012	0.034	-0.006	0.47	0.5470	0.0028	1.700	0.47
0.48	0.060	0.798	0.220	-0.018	0.008	0.059	-0.007	0.48	0.5480	0.0020	—	0.48
0.49	0.082	0.630	0.395	-0.025	0.005	0.085	-0.008	0.49	0.5513	0.0013	1.120	0.49
0.50	0.166	0.330	0.700	-0.030	0.003	0.174	-0.011	0.50	0.6235	0.0011	—	0.50
0.51	0.323	0.145	0.880	-0.025	0.002	0.335	-0.014	—	—	0.0013	0.845	0.51
0.52	0.526	0.020	0.998	-0.018	0.001	0.540	-0.015	—	—	0.0023	0.705	0.52
0.53	0.730	0.000	1.000	0.000	0.000	0.730	0.000	—	—	0.0048	0.635	0.53
0.54	0.878	-0.004	0.883	0.121	0.000	0.729	0.149	—	—	0.0094	0.635	0.54
0.55	0.960	-0.008	0.735	0.273	0.000	0.640	0.324	0.4877	0.55	0.0150	—	0.55
0.56	1.000	-0.009	0.601	0.348	0.000	0.561	0.439	0.4945	0.56	0.0220	—	0.56
0.57	0.967	-0.008	0.605	0.403	0.000	0.486	0.481	0.4959	0.57	0.0252	0.620	0.57
0.58	0.900	-0.006	0.568	0.438	0.000	0.419	0.481	0.4970	0.58	0.0268	—	0.58
0.59	0.793	-0.005	0.553	0.452	0.000	0.355	0.438	0.4972	0.59	0.0276	0.640	0.59
0.60	0.682	-0.004	0.532	0.472	0.000	0.294	0.388	0.4980	0.60	0.0278	0.680	0.60
0.61	0.555	-0.003	0.5015	0.5015	0.000	0.223	0.332	0.4983	0.61	0.0268	—	0.61
0.62	0.431	-0.002	0.408	0.594	0.000	0.136	0.295	0.4995	0.62	0.0242	0.730	0.62
0.63	0.209	-0.001	0.250	0.751	0.000	0.055	0.244	0.5009	0.63	0.0252	—	0.63
0.64	0.194	-0.001	0.100	0.901	0.000	0.013	0.181	0.5015	0.64	0.0280	0.780	0.64
0.65	0.1144	0.000	0.000	1.000	0.000	—	0.1144	0.5020	0.65	0.0330	—	0.65
0.67	0.0380	—	—	—	—	—	—	—	—	—	—	0.67
0.70	0.00638	—	—	—	—	—	—	—	—	—	—	0.70
1931 C.I.E. S_B source		0.230	0.599	0.171	Relative luminosities of trichromatic units of primaries							
$\lambda = 0.61 \mu$		-0.003	0.5015	0.5015	0.46 μ	0.53 μ	0.65 μ					
$\lambda = 0.5825 \mu$		-0.006	0.564	0.442	—	—	—					
$\lambda = 0.4940 \mu$		0.5135	0.5135	-0.027	0.0393	1.000	1.49					

Table 7. Characteristics for observer C

Wave-length λ (μ .)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients J.H.N. (1) units			Mixture curves for equal-energy spectrum			Complementary wave-lengths (μ .)		Hue-dis-crimination; just noticeable wave-length differences (μ .)	Saturation-discrimination log $\frac{L_W + L_g}{L_g}$	Wave-length λ (μ .)
		B (0.46 μ .)	G (0.53 μ .)	R (0.65 μ .)	L_B	L_g	L_R	λ	χ			
0.41	0.00278	1.006	-0.010	0.004	0.00208	-0.0004	0.0002	0.41	0.5969	—	—	0.41
0.43	0.0126	1.004	-0.006	0.002	0.0133	-0.0011	0.0004	0.43	0.5970	—	—	0.43
0.45	0.0241	1.001	-0.002	0.001	0.0245	-0.0007	0.0003	0.45	0.5972	0.0164	—	0.45
0.46	0.0407	1.000	0.000	0.000	0.0407	0.000	0.000	0.46	0.5973	0.0104	—	0.46
0.47	0.075	0.933	0.082	-0.015	0.039	0.046	-0.010	0.47	0.5988	0.0066	—	0.47
0.48	0.102	0.794	0.252	-0.046	0.024	0.101	-0.022	0.48	0.6060	0.0046	—	0.48
0.49	0.148	0.611	0.449	-0.060	0.016	0.157	-0.025	0.49	0.6328	0.0032	—	0.49
0.50	0.220	0.399	0.656	-0.055	0.0106	0.2326	-0.0232	—	—	0.0025	—	0.50
0.51	0.429	0.189	0.850	-0.039	0.0074	0.446	-0.0244	—	—	0.0023	—	0.51
0.52	0.603	0.045	0.967	-0.012	0.002	0.610	-0.009	—	—	0.0032	—	0.52
0.53	0.765	0.000	1.000	0.000	0.000	0.765	0.000	—	—	0.0054	—	0.53
0.54	0.917	-0.015	0.900	0.115	0.000	0.797	0.121	—	—	0.0093	—	0.54
0.55	0.974	-0.020	0.865	0.155	0.000	0.804	0.171	—	—	0.0164	—	0.55
0.56	0.999	-0.018	0.858	0.100	0.000	0.819	0.181	—	—	0.0208	—	0.56
0.57	0.968	-0.016	0.846	0.170	0.000	0.782	0.187	—	—	0.0212	—	0.57
0.58	0.913	-0.014	0.817	0.197	0.000	0.710	0.203	—	—	0.0184	—	0.58
0.59	0.818	-0.012	0.758	0.254	0.000	0.585	0.233	—	—	0.0143	—	0.59
0.60	0.702	-0.010	0.600	0.410	0.000	0.387	0.315	0.4735	0.60	0.0105	—	0.60
0.61	0.575	-0.008	0.504	0.594	0.000	0.262	0.313	0.4820	0.61	0.0077	—	0.61
0.62	0.462	-0.006	0.442	0.504	0.000	0.183	0.279	0.4850	0.62	0.0077	—	0.62
0.63	0.316	-0.004	0.351	0.653	0.000	0.098	0.218	0.4882	0.63	0.0097	—	0.63
0.64	0.194	-0.002	0.141	0.861	0.000	0.023	0.171	0.4930	0.64	0.0144	—	0.64
0.65	0.116	0.000	0.000	1.000	0.000	0.000	0.116	0.4940	0.65	0.0226	—	0.65
0.67	0.0324	—	—	—	—	—	—	—	—	—	—	0.67
0.70	0.00502	—	—	—	—	—	—	—	—	—	—	0.70
1931 C.I.E. S_B source		0.390	0.396	0.214	Relative luminosities of trichromatic units of primaries							
$\lambda = 0.61\mu$		-0.008	0.504	0.394	0.46 μ	0.53 μ	0.65 μ					
$\lambda = 0.5825\mu$		-0.013	0.806	0.207								
$\lambda = 0.4940\mu$		0.530	0.530	-0.060	0.0746	1.000	1.19					

Table 9. Characteristics for observer E

Wave-length λ (μ .)	Relative luminosity of equal-energy spectrum	Trichromatic coefficients J. H. N. (1) units			Mixture curves for equal-energy spectrum			Complementary wave-lengths (μ .)		Hue-dis-crimina-tion: just-noticeable wave-length dif-ferences (μ .)	Satura-tion-dis-crimina-tion log $\frac{L_W + L_g}{L_g}$	Wave-length λ (μ .)
		B (0.46 μ .)	G (0.53 μ .)	R (0.65 μ .)	L_B	L_G	L_R	λ	λ'			
0.41	0.00845	—	—	—	—	—	—	—	—	—	—	0.41
0.43	0.0166	—	—	—	—	—	—	—	—	—	—	0.43
0.45	0.0286	—	—	—	—	—	—	—	—	—	—	0.45
0.46	0.0432	1.000	0.000	0.000	0.0432	0.000	0.000	0.46	0.5548	0.0140	1.125	0.46
0.47	0.073	0.969	0.031	0.000	0.043	0.030	0.000	0.47	0.5550	0.0088	—	0.47
0.48	0.115	0.820	0.180	0.000	0.020	0.095	0.000	0.48	0.5580	0.0054	0.730	0.48
0.49	0.166	0.621	0.379	0.000	0.012	0.154	0.000	0.49	0.5671	0.0038	—	0.49
0.50	0.262	0.335	0.665	0.000	0.006	0.256	0.000	—	—	0.0034	0.585	0.50
0.51	0.456	0.119	0.881	0.000	0.003	0.453	0.000	—	—	0.0048	—	0.51
0.52	0.691	0.020	0.980	0.000	0.001	0.690	0.000	—	—	0.0078	0.555	0.52
0.53	0.845	0.000	1.000	0.000	0.000	0.845	0.000	—	—	0.0117	0.565	0.53
0.54	0.954	—0.012	0.988	0.024	0.000	0.933	0.021	—	—	0.0175	0.565	0.54
0.55	0.992	—0.020	0.900	0.120	0.000	0.882	0.110	—	—	0.0262	0.600	0.55
0.56	0.996	—0.018	0.828	0.190	0.000	0.821	0.175	0.4834	0.56	0.0303	—	0.56
0.57	0.970	—0.016	0.770	0.246	0.000	0.748	0.222	0.4913	0.57	0.0297	—	0.57
0.58	0.919	—0.014	0.736	0.278	0.000	0.681	0.238	0.4928	0.58	0.0264	0.630	0.58
0.59	0.800	—0.011	0.695	0.316	0.000	0.562	0.238	0.4943	0.59	0.0212	—	0.59
0.60	0.666	—0.009	0.614	0.395	0.000	0.416	0.250	0.4954	0.60	0.0166	0.680	0.60
0.61	0.521	—0.007	0.5035	0.5035	0.000	0.269	0.252	0.4969	0.61	0.0152	—	0.61
0.62	0.380	—0.005	0.416	0.588	0.000	0.104	0.216	0.4974	0.62	0.0155	0.720	0.62
0.63	0.256	—0.002	0.284	0.718	0.000	0.076	0.180	0.4980	0.63	0.0167	—	0.63
0.64	0.160	—0.001	0.070	0.931	0.000	0.012	0.148	0.4987	0.64	0.0188	0.750	0.64
0.65	0.0938	—	0.000	1.000	0.000	0.000	0.0938	0.4987	0.65	0.0220	0.785	0.65
0.67	0.0289	—	—	—	—	—	—	—	—	—	(0.66 μ .)	0.67
0.70	0.00307	—	—	—	—	—	—	—	—	—	—	0.70
1931 C.I.E. S_B source		0.332	0.566	0.102	Relative luminosities of trichromatic units of primaries							
$\lambda = 0.61 \mu$.		—0.007	0.5035	0.5035	0.46 μ .	0.53 μ .	0.65 μ .					
$\lambda = 0.5825 \mu$.		—0.013	0.727	0.286	—	—	—					
$\lambda = 0.4940 \mu$.		0.500	0.500	0.000	0.046	1.000	0.931					

Table 10. Characteristics for observer F

Wave-length λ (μ .)	Relative uminosity of equal- energy spectrum	—0.042	0.018	0.025	—0.019	0.007	0.41	0.	ue-dis- ting- uish- able wave- length dif- ferences (μ .)	Satura- tion-dis- crimina- tion log $L_W + L_S$
0.41	0.013	1.024	0.018	0.025	—0.019	0.007	0.41	0.	0.41	
0.43	0.022	—0.038	0.015	0.040	—0.028	0.010	0.43	0.	0.43	
0.45	0.037	—0.023	0.003	0.059	—0.025	0.003	0.45	0.	0.45	
0.46	0.051	0.000	0.000	0.051	0.000	0.00	0.46	0.	0.46	
0.47	0.062	0.058	—0.015	0.033	0.038	—0.019	0.47	0.	0.47	
0.48	0.095	0.864	—0.024	0.024	0.083	—0.011	0.48	0.	0.48	
0.49	0.157	0.662	—0.062	0.014	0.166	—0.023	0.49	0.	0.49	
0.50	0.261	0.400	—0.078	0.007	0.281	—0.027	—	—	0.50	
0.51	0.420	0.738	—0.050	0.003	0.439	—0.022	—	—	0.51	
0.52	0.611	0.915	—0.020	0.001	0.621	—0.011	—	—	0.52	
0.53	0.770	0.988	0.000	0.000	0.770	0.000	—	—	0.53	
0.54	0.906	1.000	0.059	0.	0.859	0.047	—	—	0.54	
0.55	0.972	0.960	0.103	0.	0.882	0.090	—	—	0.55	
0.56	0.999	0.918	0.139	0.	0.874	0.125	—	—	0.56	
0.57	0.966	0.880	0.175	0.	0.813	0.153	—	—	0.57	
0.58	0.900	0.841	0.206	0.	0.731	0.169	—	—	0.58	
0.59	0.788	0.807	0.285	0.389	0.581	0.207	0.4790	0.59	0.59	
0.60	0.641	0.725	0.389	0.503	0.469	0.232	0.4875	0.60	0.60	
0.61	0.495	0.619	0.503	0.796	0.260	0.235	0.4907	0.61	0.61	
0.62	0.361	0.503	0.687	0.801	0.122	0.239	0.4929	0.62	0.62	
0.63	0.244	0.317	0.801	0.901	0.053	0.191	0.4937	0.63	0.63	
0.64	0.153	0.201	0.901	—	0.017	0.136	0.4941	0.64	0.64	
0.65	0.096	0.100	—	—	0.000	0.096	0.4948	0.65	0.65	
0.67	0.0347	0.000	—	—	—	—	—	—	0.67	
—	0.00318	—	—	—	—	—	—	—	0.70	

0. 4

 $\lambda = 0.61 \mu$. $\lambda = 0.5825 \mu$. $\lambda = 0.4940 \mu$.

—0.006

—0.012

0.540

.503

.796

540

0. 4

0.503

0.210

—0.080

Table 11. Characteristics for observer L

Wave-length λ (μ .)	Relative luminosity of equal- energy spectrum	Trichromatic coefficients J.H.N. (2) units			Mixture curves for equal-energy spectrum				Complementary wave-lengths (μ .)		Hue-dis- crimina- tion; just- noticeable wave- length dif- ferences (μ .)	Satura- tion-dis- crimina- tion log $\frac{L_W + L_S}{L_S}$	Wave- length λ (μ .)
		B (0.46 μ .)	G (0.53 μ .)	R (0.65 μ .)	L _B	L _G	L _R	λ	λ'				
0.41	0.011	1.040	-0.055	0.015	0.023	-0.012	0.000	0.41	0.5819	—	—	—	0.41
0.43	0.035	1.026	-0.035	0.009	0.055	-0.020	0.000	0.43	0.5823	0.0100 (0.44)	—	—	0.43
0.45	0.0624	1.014	-0.017	0.003	0.0764	-0.014	0.000	0.45	0.5827	0.0081	—	—	0.45
0.46	0.0994	1.000	0.000	0.000	0.0994	0.000	0.000	0.46	0.5830	0.0063	—	—	0.46
0.47	0.145	0.960	0.065	-0.025	0.085	0.063	0.000	0.47	0.5832	0.0046	—	—	0.47
0.48	0.176	0.890	0.195	-0.085	0.054	0.128	0.000	0.48	0.5913	0.0031	—	—	0.48
0.49	0.218	0.795	0.315	-0.250	0.026	0.202	0.000	0.49	0.6350	0.0018	—	—	0.49
0.50	0.312	0.630	0.430	-0.870	0.014	0.309	0.000	—	—	0.0013	—	—	0.50
0.51	0.508	0.170	1.030	-0.200	0.008	0.510	0.000	—	—	0.0013	—	—	0.51
0.52	0.723	0.055	1.045	-0.100	0.004	0.726	0.000	—	—	0.0018	—	—	0.52
0.53	0.890	0.000	1.000	0.000	0.000	0.890	0.000	—	—	0.0036	—	—	0.53
0.54	0.901	0.010	0.920	0.090	0.000	0.981	0.010	—	—	0.0062	—	—	0.54
0.55	0.988	-0.014	0.786	0.228	0.000	0.960	0.028	—	—	0.0090	—	—	0.55
0.56	0.945	-0.012	0.600	0.412	0.000	0.884	0.061	—	—	0.0112	—	—	0.56
0.57	0.815	-0.011	0.471	0.600	0.000	0.711	0.104	—	—	0.0120	—	—	0.57
0.58	0.641	-0.010	0.300	0.710	0.000	0.518	0.123	—	—	0.0106	—	—	0.58
0.59	0.448	-0.008	0.204	0.804	0.000	0.321	0.127	0.4783	0.59	0.0071	—	—	0.59
0.60	0.281	-0.007	0.142	0.865	0.000	0.175	0.106	0.4838	0.60	0.0052	—	—	0.60
0.61	0.178	-0.006	0.091	0.915	0.000	0.080	0.089	0.4870	0.61	0.0043	—	—	0.61
0.62	0.0991	-0.004	0.046	0.958	0.000	0.016	0.075	0.4887	0.62	0.0036	—	—	0.62
0.63	0.0529	-0.002	0.015	0.987	0.000	0.0053	0.0476	0.4898	0.63	0.0034	—	—	0.63
0.64	0.0298	-0.001	0.005	0.996	0.000	0.0014	0.0284	0.4902	0.64	0.0040	—	—	0.64
0.65	0.0131	0.000	-0.003	1.000	0.000	0.000	0.0131	0.4904	0.65	0.0058	—	—	0.65
0.67	0.00318	0.000	-0.003	1.000	0.000	-0.00009	0.00337	—	—	—	—	—	0.67
0.70	0.00041	0.000	-0.004	1.004	0.000	-0.00002	0.00043	0.4907	0.70	—	—	—	0.70
1931 C.I.E. S_B source		0.264	0.194	0.542	Relative luminosities of trichromatic units of primaries								
$\lambda = 0.61 \mu$.		-0.006	0.091	0.915	0.46 μ .	0.53 μ .	0.65 μ .						
$\lambda = 0.5825 \mu$.		-0.010	0.075	0.735	0.095	1.000	0.100						
$\lambda = 0.4940 \mu$.		0.058	0.658	-0.316									

DISCUSSION

Dr W. D. WRIGHT. This paper provides the most exhaustive analysis of anomalous trichromatism that has yet been reported. Moreover, the Physical Society has been well advised in waiving its usual practice so far as to publish both diagrams and tables for the characteristics of each observer. For any quantitative examination of the results the tables are essential, but the diagrams are equally valuable for a more general discussion of the various types of observer that are found.

The results on saturation-discrimination are of special interest, for I believe that they are the first measurements on anomalous trichromats to have been published. The value of the data as a whole is twofold. In the first place the results are of theoretical interest and importance as showing precisely the variations from normal vision that do occur, and this knowledge should lead to a further elucidation of the visual processes. In particular, theoretical attempts to relate one characteristic to another, for instance the hue-discrimination curve and the mixture curves, can now be applied to a number of different visual mechanisms, and any theory can now be put to a correspondingly more stringent test. In this connexion it should be realized that the theoretical manipulation of the data is not likely to yield results of any importance unless they are expressed in terms of some fundamental primaries or responses. At present the values have been tabulated in terms of the instrument primaries that were used. I should like to ask the author whether he would expect some of the rather irregular bumps that occur on the mixture curves to disappear if the results were transformed to a new set of primaries, or whether they are an inherent part of the curves.

The second general use to which the results can be put is the practical evaluation of the degree of deficiency to which an observer is subject and the consequent extent to which his activities should be limited. The anomalous-trichromat group is especially important because it includes the borderline cases between the normal and the abnormal, and they are the persons who might be liable to be rejected from certain occupations when in practice their inclusion would be quite safe or, alternatively, they might be included when they should have been excluded. The recognition and elimination of dichromats is comparatively easy, but the decision whether a person is merely an extreme variation from the normal, or actually slightly anomalous, may be very difficult.

To understand what is involved, it would be of very material aid if some picture could be obtained of the sensations which the colour-blind person perceived in terms of those of which the normal person is conscious. Suppose, for instance, we were prepared to assume that the blue and yellow radiations produced the same sensation for both types of observer, then it should be possible to relate all the colour sensations of the anomalous observer with those of the normal observer, by stepping off the discrimination steps from the blue and the yellow. It should, in fact, be possible to plot the spectrum locus for the anomalous observer in the normal colour triangle, and in the limit this locus would reduce to the straight line that is found for the dichromat. This would provide a very convenient way of demonstrating the gradation from one form of colour-vision to another, and would be of value in

estimating the degree of abnormality exhibited by an observer. If, in addition, it were found that the spectrum locus as derived from discrimination data also represented the colour-mixture results to a reasonable degree of accuracy, it would be a fact of very considerable theoretical importance. It would be interesting to know whether the author has attempted any calculations on these lines, and if so, the extent to which he has been successful.

AUTHOR'S reply. As regards the irregularities in the mixture curves, I think that those just by a primary would be affected by a change of primaries, but not those removed from a primary. The mixture curves for observer C have been referred to the fundamental responses given by Dr Wright,* and the irregularity at 0.69μ . still persists. However, without some experimental evidence it does not seem justifiable to assume that these fundamental responses are applicable to an anomalous observer.

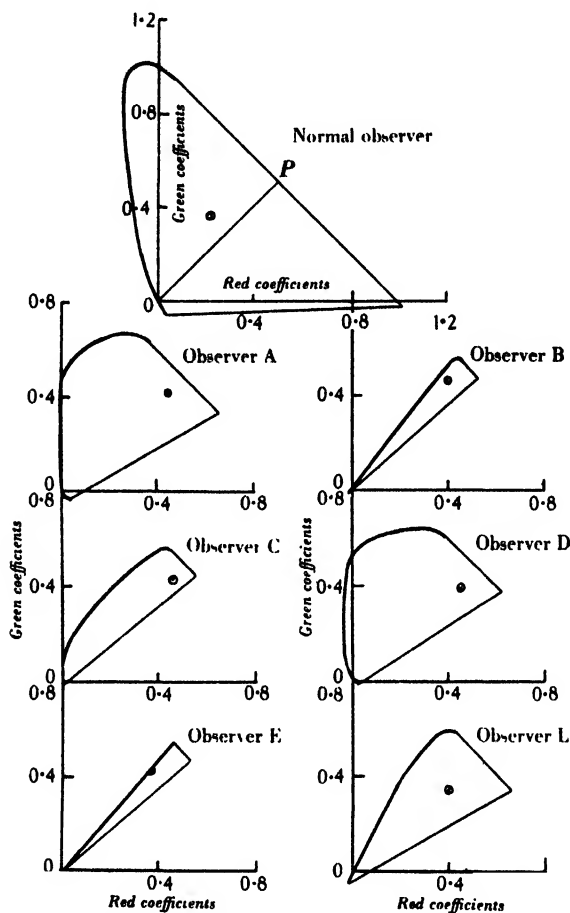
The existence of the irregularities in the relation between the complementary wave-lengths in the case of observer C would lead one to suspect that they are of a fundamental nature.

With regard to Dr Wright's suggestion as to finding some relation between the normal and anomalous sensations, some tentative work was done on these lines. From the saturation-discrimination data obtained for observers B, C, and D, it was seen that the spectrum colours in the red-yellow-green region appeared very desaturated in comparison with the normal, and that the saturation corresponded approximately to the minimum for the normal in the region. This is clearly in agreement with the hue-discrimination data, and may be taken to confirm the suggestion put forward by Wright in Pitt's report⁽¹⁾, that the anomalous observer sees red and green as desaturated orange and yellow-green respectively. Working from this fact an attempt has been made to obtain a picture of the appearance of the spectrum to the anomalous observer in terms of normal sensations. The area of the colour-triangle for the normal observer represents a definite number of distinguishable colours, while the straight line to which the colour triangle for the dichromat reduces also represents a certain smaller number of distinguishable colours. Now the anomalous trichromat can see more colours than the dichromat, but fewer than the normal. Hence, to give a subjective representation of the number of colours, the anomalous trichromat should have a colour triangle smaller than the normal and yet larger than the dichromat. If, however, the anomalous colour triangles are plotted relative to the same physical stimuli as the normal, it is clear that the triangles must always be of the same order of size. It is therefore necessary to devise some method by which the triangles may be expressed in terms of the same subjective stimuli as the normal. We have seen above that it is reasonable to suppose that the anomalous trichromat sees red and green as desaturated orange and yellow-green. Now if we extend this by saying that the sensation of yellow is the same for both normal and anomalous trichromat, then there is one point at which we may fix the anomalous subjective colour triangle relative to the normal. If at the same time we assume, as in McDougall's evolutionary theory, that the blue sensations are the same in each case, then we can say that the straight line of

* Wright, W. D. *Proc. Roy. Soc. B*, 115, 49-87 (1934).

the dichromat should be drawn between the blue and the yellow of the normal triangle, and that the anomalous triangles should be drawn about this line and between it and the normal triangle.

If now, starting from the yellow and working towards either the red or the green, we suppose that one hue-discrimination step will produce the same change in colour, whether it is for the normal or for the anomalous trichromat, then by finding the



Reduced colour triangles for Observers A, B, C, D, E and L compared with normal.

⊙ = S_B : OP = Straight line for dichromat.

number of steps for the anomalous trichromat between the yellow and 0.65μ ., we may say that this corresponds in colour sensation to a colour distant from the yellow, in the normal case, by the same number of hue-discrimination steps. In this way it is possible to obtain two wave-lengths in the normal spectrum to which 0.65μ . and 0.53μ . in the anomalous spectrum correspond in colour. In the yellow region the assumptions involved in the above procedure would seem to be justified, at least as a first approximation. It is, however, necessary to make the further assumption that the changes which have been made are also applicable in the blue-green region.

For convenience the yellow chosen was at 0.5825μ . and the colour triangles of all the anomalous observers were referred to the W.D.W. system. In each case the numbers of colour steps between 0.5825μ . and 0.53μ . and 0.65μ . were determined from the hue-discrimination curve for the observer. From this latter, and from the characteristics of the normal observer, the coefficients of the colours in the normal triangle corresponding to 0.53μ . and 0.65μ . in the anomalous triangle, were found. This gave the new coefficients for the red and the green primaries, and the modified coefficients for the remaining wave-lengths were determined by the appropriate transformations.

The transformation is in reality equivalent to referring the anomalous triangles to a set of primaries R_A , G_A and B_A . If the normal primaries are R_N , G_N and B_N , then from the hue-discrimination we have

$$\left. \begin{aligned} C_{A\ 0.65\mu} &= C_N = aR_N + bG_N \\ C_{A\ 0.53\mu} &= C_N = a'R_N + b'R_N \end{aligned} \right\}$$

where C_A is the colour for the anomalous and C_N for the normal.

Then the new primaries R_A and G_A are chosen so that

$$\left. \begin{aligned} C_{N\ 0.65\mu} &= aR_A + bG_A = R_N, \\ C_{N\ 0.53\mu} &= a'R_A + b'G_A = G_N. \end{aligned} \right\}$$

Further we say

$$C_{A\ 0.5825\mu} = C_{N\ 0.5825\mu}.$$

and

$$0.5R_A + 0.5G_A = 0.5R_N + 0.5G_N;$$

also

$$B_N = B_A.$$

For example, in the case of observer A, the number of steps between 0.5825μ . and 0.65μ . is 15.52, and that between 0.5825μ . and 0.53μ . is 8.92, as compared with the normal values of 48.64 and 30.67.

From the curves we find

$$\left. \begin{aligned} C_{A\ 0.65\mu} &= C_{N\ 0.5825\mu} = 0.662R_N + 0.338G_N \quad (\text{the blue being neglected}), \\ C_{A\ 0.53\mu} &= C_{N\ 0.5716\mu} = 0.366R_N + 0.634G_N. \end{aligned} \right\}$$

From this we choose the primaries so that

$$\left. \begin{aligned} C_{N\ 0.65\mu} &= 0.662R_A + 0.338G_A = R_N, \\ C_{N\ 0.53\mu} &= 0.366R_A + 0.634G_A = G_N, \end{aligned} \right\}$$

and solving for R_A and G_A we find that the anomalous primaries are

$$\left. \begin{aligned} R_A &= 2.142R_N - 1.142G_N, \\ G_A &= -1.237R_N + 2.237G_N, \\ B_A &= B_N. \end{aligned} \right\}$$

As such, the triangles are a perfectly legitimate means of expressing the coefficients of the anomalous observers. If, however, the triangles are to be considered as a subjective representation of the colour sensations of the anomalous trichromat in comparison with the normal, then it is necessary to consider the assumptions made in deriving them. These assumptions are: (1) that the sensation of yellow is the same for both normal and anomalous trichromats; (2) that the yellow occurs in

the same place in the spectrum for all observers, and is at 0.5825μ .; (3) that one hue-discrimination step will correspond to the same change in sensation, whether it is for the normal or for the anomalous trichromat; and (4) that the sole differences between normal and anomalous trichromats are due to change in the red and green sensations, and that the blue is the same for both.

Examining these assumptions, we note that the first necessitates that the sensations experienced by the normal and anomalous trichromats shall be comparable. This type of assumption cannot be proved or disproved, and it is only possible to consider the probability of its being true. The second assumption is definitely only a first approximation, since it was seen that the positions of the pure yellow differed slightly for normal and anomalous trichromats. The use of 0.5825μ . is again an approximation, the value being chosen merely for convenience. The assumption that a hue-discrimination step means the same change in sensation for both normal and anomalous trichromats is of the same type as the first, but if the first may be made this assumption should not introduce any large error, at least in the yellow region. The last assumption is probably the largest source of error in deriving the triangles. The characteristics have shown that the differences between normal and anomalous trichromats are not confined to the yellow region nor yet to the red and green sensations entirely. For example, if they were so confined, the hue-discrimination in the blue-green region for observer B should be poor, while in fact it is comparable with the normal.

The reduced triangles must therefore be considered only as representing the anomalous sensations in terms of the normal within the limitations imposed by the assumptions.

A rigorous test of the validity of the triangles, assuming the sensations to be comparable, would necessitate a large amount of saturation-discrimination data. If, however, we compare the saturation-discrimination of the normal and observer D in the blue-green region with the distance between the white point and the spectral locus, we can see that an approximately proportionate reduction has taken place. On the other hand, in the case of observer B, where the saturation-discrimination is nearly normal, the reduced triangle is very narrow and in consequence the agreement is poor. The suggestion that the reduced triangles represent the anomalous sensations in terms of the normal, or that it is possible to draw such triangles by any similar method, implies that the anomalous trichromats have different fundamental sensations and yet the same physiological mechanism as the normal. Thus, in the case of observer D, where the saturation-discrimination supplies a favourable test, it can be said that the assumptions are to some extent justified; on the other hand, in the case of observer B, where the agreement is poor, it can definitely be said that the assumptions are not justified, and similar considerations would apply to observer E. The possibility of there being two mechanisms, either coexistent or alternative, has been present throughout, and while, as has been stressed, the reduced triangles must not be used as theoretical proof, they do in this case offer at least a feasible theory as to the nature of the two mechanisms, namely, a change in fundamental sensations, and a change in the physiological perception mechanism.

HEAT-CONDUCTION IN A MEDIUM HAVING THERMAL PROPERTIES DEPENDING ON THE TEMPERATURE

By M. R. HOPKINS, M.Sc.

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ABSTRACT. Typical standard calculations in the theory of heat-conduction are modified to allow for the variation of the thermal properties of the medium with temperature.

WE consider a region V of the medium, either extending to infinity or confined by given boundaries. Let $h(x, y, z)$ be the initial temperature of the medium, $H(x, y, z, t)$ the temperature of the boundaries, if any, and $Q(x, y, z, t)$ the rate of generation of heat per unit volume. If we write k for the conductivity and c for the product of the specific heat and density, the equation is

$$c\theta - \text{div} \{k \text{ grad } \theta\} = Q \quad \dots\dots(1),$$

where θ is the temperature and θ means $\partial\theta/\partial t$.

Let $\Theta(x, y, z, t)$ be the solution of the problem obtained by assuming that c and k have constant values c_0 and k_0 , the equation thus reducing to

$$L[\theta] = Q \quad \dots\dots(2),$$

where
$$L = c_0 \frac{\partial}{\partial t} - k_0 \text{ div grad}.$$

Θ is, of course, the standard solution, worked out for a variety of cases in the textbooks on heat-conduction.

Provided c/k is independent of temperature the solution of (1) can be obtained at once by the methods used to determine Θ ; for if $c/c_0 = k/k_0 = p(\theta)$, say, where c_0 and k_0 are the values at any arbitrary temperature, and if we write

$$\phi = \int_{\theta_0}^{\theta} p(\theta) d\theta,$$

where θ_0 is any arbitrary temperature, then the initial and boundary values of ϕ , say $h'(x, y, z)$ and $H'(x, y, z, t)$, are obtained by setting h and H as the upper limit of the integral; moreover one can easily show that the equation satisfied by ϕ is obtained from (2) on replacing θ by ϕ . Thus from the expression for Θ in terms of h , H , and Q , we obtain ϕ on replacing h and H by h' and H' .

Though we shall find this result useful, we must, for practical purposes, assume no such relationship between c and k . Let us write

$$c = c_0 \{1 + \mu f(\theta)\} \quad \text{and} \quad k = k_0 \{1 + \mu F(\theta)\}.$$

Then the equation is

$$L[\theta] = Q + \mu [k_0 \operatorname{div} \{F(\theta) \operatorname{grad} \theta\} - c_0 f(\theta) \theta] \quad \dots\dots(3).$$

If we think of the whole expression in the bracket as $G(x, y, z, t)$, we may note that the same equation would arise if heat were generated at the rate $Q + \mu G$ per unit volume in a medium in which c and k had the values c_0 and k_0 . In the latter medium let $g(x, y, z, x', y', z', t - \tau)$ be the Green's function for zero boundary temperature, that is, the temperature at co-ordinates x, y, z and time t due to the generation of unit quantity of heat at x', y', z' and τ , the boundaries being kept at temperature zero. Then the required solution is evidently

$$\Theta + \mu \int_V \int_0^t g \cdot G(x', y', z', \tau) dx' dy' dz' d\tau \quad \dots\dots(4).$$

Regarding the term in μ as a correction effect, we evaluate it approximately by writing the known function Θ instead of θ in G . It is to be noted that g is a known function which, even if Q is zero, will have arisen in the calculation of Θ . If, owing to symmetry, only an integral of g with respect to the dashed co-ordinates (perhaps over a plane or a spherical shell) has arisen in the calculation of Θ , the same integral will suffice for calculating the correction term.

If we think of the solution as a power series in μ , the coefficients of the higher powers can be evaluated similarly by the aid of the Green's function. At every stage of the approximation the initial and boundary values will be those of the principal term Θ , and these are the values prescribed. In a few very simple cases the equations determining the coefficients of the powers of μ can be solved directly, without the aid of a Green's function.

In many cases it will be sufficiently accurate to regard c and k as linear in the temperature, so that we can write $\mu f(\theta) = \mu_1 \theta$ and $\mu F(\theta) = \mu_2 \theta$. The solution as far as the first power of the μ 's will then be of the form $\Theta + \mu_1 \psi_1 + \mu_2 \psi_2$. It will sometimes be quicker to evaluate only one of the two functions ψ_1 and ψ_2 by the above method; the other can then be deduced, since the sum of the two is readily obtained by setting $\mu_1 = \mu_2$, thus obtaining a medium in which c/k is independent of temperature, for which the exact solution, and hence $\psi_1 + \psi_2$, is given by the theorem stated earlier in the paper.

We turn now to some typical applications. The results only will be given, since the calculations are straightforward and of little interest.

(1) A sheet of infinite area, bounded by the planes $x=0$ and $x=d$, is at temperature θ_0 at time zero, and its surfaces are kept always at temperature zero. We take the linear form mentioned above for c and k , and we assume that $\mu_1 \theta_0$ and $\mu_2 \theta_0$ are not large fractions. We then apply equation (4), and for the calculation we require, not, of course, the Green's function itself, but only the solution for an instantaneous plane source with boundary temperature zero. Putting $\kappa^2 = k_0/c_0$, we find for the temperature at x and t

$$\sum_{n, m, p} \frac{4\theta_0 \sin n_1 x}{0} \left\{ \frac{e^{-n_1^2 \kappa^2 t}}{n_1 d} - \frac{16\theta_0 n_1 [\mu_1 (m_1^2 + p_1^2) - \mu_2 n_1^2] [e^{-(m_1^2 + p_1^2) \kappa^2 t} - e^{-n_1^2 \kappa^2 t}]}{d^3 [(m_1 + p_1)^2 - n_1^2] [(m_1 - p_1)^2 - n_1^2] [m_1^2 + p_1^2 - n_1^2]} \right\}.$$

Here $n_1 = (2n+1)\pi/d$, and m_1 and p_1 are similarly defined in terms of m and p . When t is very great the temperature is practically the same as if c and k had the values c_0 and k_0 and either the initial conditions were established at a time differing somewhat from zero or the initial temperature differed somewhat from θ_0 .

(2) As an example, using non-linear expressions for c and k we will take the case of a semi-infinite medium initially at uniform temperature θ_0 and having the boundary kept at zero temperature. This case is the subject of a paper by J. H. Awbery⁽¹⁾, who shows that the solution will contain x and t only in the form x/\sqrt{t} , the partial differential equation of heat-conduction thus reducing in this case to an ordinary differential equation. Except in the case when c/k is constant his solution of this equation is, however, open to a criticism as regards its utility, for it contains, not the initial temperature, but a parameter the value of which in terms of the initial temperature and the thermal coefficients remains unspecified, owing to the solution, which contains a power series in x/\sqrt{t} , failing at large values of the variable and hence at the initial state. Our method, which here reduces to a direct integration without the aid of a Green's function, gives

$$\theta = \theta_0 I + \mu \theta_0^2 \left[\frac{1}{2} \beta (I - I^2) + \gamma (1 - E^2 - I - \gamma EI) \right] \\ + \mu^2 \theta_0^3 \left[\frac{1}{2} \beta^2 (I^3 - I^2) + \beta \gamma F + \gamma^2 G + \frac{1}{3} \beta_1 (I - I^3) + \gamma_1 H \right],$$

where $y = x\sqrt{\pi}/2\kappa\sqrt{t}$; $c = c_0(1 + \mu\alpha\theta + \mu^2\alpha_1\theta^2)$; $k = k_0(1 + \mu\beta\theta + \mu^2\beta_1\theta^2)$;

$$\gamma = (\beta - \alpha)/\pi; \quad \gamma_1 = (\beta_1 - \alpha_1)/\pi; \quad E = e^{-y^2/\pi};$$

$$F = 1 - E^2 - (2 + \gamma E - 4E^2) I + (1 + \frac{5}{2}\gamma E) I^2 - 3\sqrt{3} (I_1 - I)/2;$$

$$G = -2(1 - E^2) - \gamma(E + \frac{1}{2}E^3) + \{2 + 2\gamma E - (\pi + \gamma^2) E^2\} I - \frac{1}{4}(\pi + 2\gamma^2) \gamma EI^2 \\ + \frac{3}{4}\sqrt{3}\pi (I_1 - I);$$

$$H = -2E^2 I - \gamma EI^2 + \sqrt{3} (I_1 - I).$$

I signifies $I(y/\sqrt{\pi})$ defined as $\frac{2}{\sqrt{\pi}} \int_0^{y/\sqrt{\pi}} e^{-u^2} du$ and I_1 is $I(y/\sqrt{3})$. The calculation is carried as far as the terms in μ^2 .

(3) For the next example let us create an artificial difficulty by choosing a case of a hypothetical nature having initially an infinite temperature in an infinitesimal region; such a case may evidently give rise to difficulties of convergence. We shall take, in fact, the instantaneous plane source generating suddenly, at time zero, in an infinite medium at temperature zero, a quantity of heat Q per unit area of the plane $x=0$, thus producing instantaneously an infinite temperature there. If we use the linear form for c and k , the calculation as far as the first power of the μ 's gives

$$\theta = At^{-\frac{1}{2}} E \left[1 + \frac{1}{2} At^{-\frac{1}{2}} \{(\mu_2 - \mu_1) \gamma I - \mu_2 E\} \right],$$

where E and I are as in the previous example and A is $Q/2\kappa c_0 \sqrt{\pi}$. For small values of the μ 's the correction term is only a small fraction of the whole throughout a certain range of x and t , and the approximation there is probably a good one; it certainly is if $\mu_1 = \mu_2$, as is easily shown by writing down the exact solution for that case. The infinite initial temperature does not arise, of course, in any real physical problem.

(4) In conclusion a case in which the surface temperature is varied with time has been considered. The calculations are found to give no particular difficulty, but the expression obtained is naturally rather cumbrous and is hardly of sufficient interest to be given here.

I am indebted to Dr P. M. Davidson for supplying me with the general method described above, together with the calculations for a typical case, the cooling of a sphere, which had arisen in some experimental work.

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THE PRINCIPAL PARAMAGNETIC SUSCEPTIBILITIES OF POTASSIUM FERRICYANIDE AT LOW TEMPERATURES

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ABSTRACT. The author's previous measurements of the principal magnetic susceptibilities of potassium ferricyanide have been repeated and extended to a temperature of 14.2°K . Two of the principal susceptibilities are approximately equal throughout the whole temperature range from 290 to 14°K ., but that along the third principal axis is considerably smaller. The anisotropy is almost 400 per cent at 14°K . and is still increasing as the temperature falls. A brief comparison with Howard's theory of the magnetic properties of $\text{K}_3[\text{Fe}(\text{CN})_6]$ is made.

§ 1. INTRODUCTION

IN 1933 some measurements were published of the principal susceptibilities of the paramagnetic crystal, potassium ferricyanide, over the temperature range from 290 to 75°K .⁽¹⁾ The main features of the results, the low magnetic moment and the high anisotropy of the crystal, later received a very satisfactory explanation at the hands of J. B. Howard⁽²⁾. It seemed of considerable interest to extend the measurements to lower temperatures as opportunity permitted and to compare them with the theory. The results for the temperature range from 290 to 14°K . are presented below.

§ 2. EXPERIMENTAL PROCEDURE AND RESULTS

The susceptibilities were determined with the aid of the same apparatus as before, a Sucksmith magnetic balance adapted for use at low temperatures. These temperatures were obtained with suitable liquefied gases boiling under atmospheric or reduced pressure, viz. methyl chloride, ethylene, oxygen and hydrogen. Since the crystals of potassium ferricyanide, though actually monoclinic, are very nearly orthorhombic ($\beta = 90^\circ 6'$) and since the previous determinations had shown that the magnetic properties also are in agreement with this fact, measurements were made in the work now described of the susceptibilities along three mutually perpendicular directions in the crystal, one perpendicular to the plane (100), another perpendicular to the plane (010), and one parallel to the c axis. These susceptibilities will then represent the three principal susceptibilities of the crystal with an accuracy of 1 or 2 per cent, which is quite adequate for the present results.

The results of the measurements are given in tables 1, 2 and 3.

Table 1. χ_1 , viz. χ perpendicular to the (100) plane

T ($^{\circ}$ K.)	$\chi_1 \times 10^6$	χ'_{1m}	$1/\chi'_{1m}$	μ_{1B}^2
289.7	7.47	0.00260	385	6.07
248.9	8.51	0.00294	340	5.90
208.0	10.04	0.00344	291	5.77
169.7	12.21	0.00416	240	5.69
117.9	16.44	0.00555	180	5.28
90.1	20.28	0.00680	147	4.94
74.3	23.04	0.00772	130	4.73
63.9	26.58	0.00887	113	4.57
20.5	72.78	0.02408	41.5	3.97
17.0	85.37	0.02824	35.4	3.87
14.6	97.28	0.03214	31.1	3.78

Table 2. χ_2 , viz. χ parallel to the c axis

T ($^{\circ}$ K.)	$\chi_2 \times 10^6$	χ'_{2m}	$1/\chi'_{2m}$	μ_{2B}^2
291.9	6.31	0.00222	450	5.22
273.2	6.68	0.00234	427	5.15
248.8	7.00	0.00244	410	4.90
221.2	7.54	0.00263	380	4.69
179.2	8.48	0.00292	342	4.22
169.6	8.70	0.00300	333	4.10
144.0	9.47	0.00326	307	3.78
117.0	10.34	0.00354	282	3.35
90.2	11.38	0.00388	258	2.82
75.5	12.00	0.00409	244	2.48
63.8	12.54	0.00428	234	2.20
20.4	21.11	0.00709	141	1.16
17.0	23.89	0.00800	125	1.09
14.2	27.04	0.00904	111	1.03

Table 3. χ_3 , viz. χ perpendicular to the (010) plane

T ($^{\circ}$ K.)	$\chi_3 \times 10^6$	χ'_{3m}	$1/\chi'_{3m}$	μ_{3B}^2
289.5	7.00	0.00244	410	5.69
248.9	8.08	0.00278	360	5.58
217.8	9.07	0.00313	320	5.49
195.8	9.98	0.00342	292	5.39
169.3	11.43	0.00390	256	5.32
120.7	15.21	0.00515	194	5.01
90.1	19.89	0.00669	149	4.86
76.2	23.10	0.00774	129	4.75
64.1	26.37	0.00882	113	4.56
20.4	75.04	0.02503	40.0	4.11
17.1	89.50	0.02959	33.8	4.08
14.0	107.9	0.03565	28.0	4.02

In the above tables χ_1 , in accordance with the usual convention, is the larger of the principal susceptibilities in the ac plane and χ_3 is the one along the axis of symmetry. χ'_m is the molecular susceptibility corrected for the diamagnetism of the molecule.* μ_B is the effective Bohr magneton number calculated from $\mu_B = 2.839 \sqrt{(\chi'_m T)}$.

* The correction applied for the diamagnetic properties of the molecule was 140×10^{-6} , obtained from $K^+ = -18.5 \times 10^{-6}$, $CN^- = -10.8 \times 10^{-6}$, $Fe^{+++} = -20 \times 10^{-6}$. See E. C. Stoner, *Magnetism and Matter*, p. 470.

§ 3. DISCUSSION

The present results are in good agreement with those of the previous measurements, this being all the more satisfactory since the new determinations were made on a crystal grown from another specimen of the salt of different origin. (The kink previously suspected in the χ_2 curve eventually proved to be spurious.)

It will be seen that χ_1 and χ_3 are almost equal throughout the whole temperature range and that the $\{1/\chi, T\}$ curves for these quantities cross between 60° and 70° K. On the other hand, χ_2 diverges more and more from χ_1 and χ_3 as the temperature falls. In other words the anisotropy of the crystal becomes more pronounced at low temperatures, reaching the surprisingly large value of 400 per cent at 14.2° K. The crystal is thus almost uniaxial at the lowest temperatures.

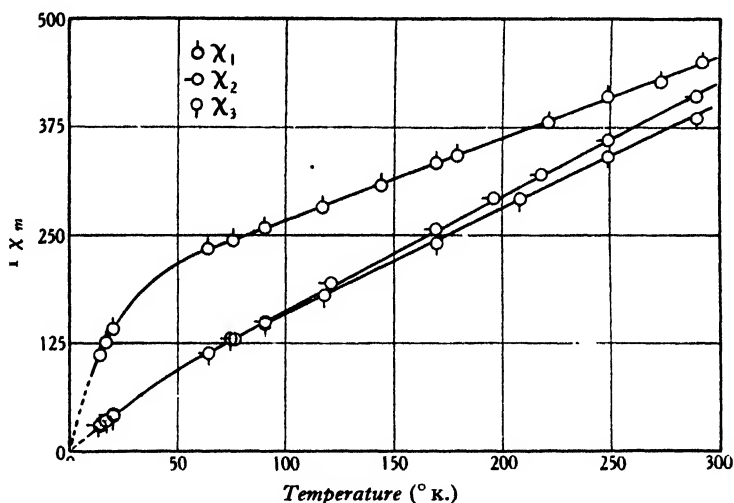


Figure 1. The principal susceptibilities of potassium ferricyanide.

Howard's theory of the author's earlier results for potassium ferricyanide may be summarized as follows. The Fe^{+++} ion is regarded as being situated in a very high electrostatic field of cubic symmetry (due to the CN groups) on which is superposed a smaller field of rhombic, almost axial, symmetry. Under the action of the cubic field the coupling of the individual l 's of the five electrons of Fe^{+++} to a resultant orbital angular momentum L is destroyed, and the lowest level of the unperturbed ion (electron spin being neglected) splits into a triply degenerate level d_e and a doubly degenerate level d_γ . For an octahedral arrangement of the CN groups, the d_e level will lie lower. Further, it is assumed that the d_γ level will be situated so high that its contribution to the susceptibility can be neglected. The rhombic field now splits the d_e level into three levels which, on the introduction of the electron spin, are all doubly degenerate. There are five electrons to fit into these three levels so that two will be doubly occupied and, by the Pauli principle, will contribute nothing to the susceptibility. The fifth electron has a free spin so that

the magnetic properties will correspond to $S = \frac{1}{2}$ if one can neglect orbital contributions to the susceptibility. Howard, however, shows that the latter cannot be wholly neglected and introduces a coupling coefficient between l and s to allow for this fact. A knowledge of the positions of the six levels which exist in the presence of a magnetic field then enables one to calculate the susceptibility. The low value of the magnetic moment and the high magnetic anisotropy are satisfactorily explained by a suitable choice of the coupling coefficient and the coefficients of the rhombic field.

Howard's published curves for μ_B^2 against T only extend to 75°K . A continuation of his calculations to lower temperatures shows that the value of μ_B^2 for both χ_1 and χ_3 at the absolute zero is about 4.0. A comparison with the values given in the present tables shows that Howard's theoretical curves are in reasonable agreement with the experimental results over the whole temperature range yet covered. This is not, however, the case for χ_2 . The theoretical value for μ_B^2 at 0°K . is about 2.0, whereas the experimental value at 14.2°K . is already as low as 1.0.

It is not, however, opportune at present to make a detailed comparison between the experimental results and Howard's theory. The latter is essentially a theory of the magnetic behaviour of the $[\text{Fe}(\text{CN})_6]$ complex whereas the experimental results for the crystal give only the minimum anisotropy of these magnetic units. The $[\text{Fe}(\text{CN})_6]$ groups may be variously situated relative to each other in the crystal lattice, and a detailed knowledge of the structure of the crystal is required before one can calculate the anisotropy of the magnetic units from the observed anisotropy of the crystal as a whole. It is known that there are four molecules in the unit cell of the $\text{K}_3[\text{Fe}(\text{CN})_6]$ lattice, but the actual positions of the CN groups are not yet known. A comparison with Howard's theory can be undertaken when this information becomes available.

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A NOTE ON THE SPECTRUM OF CADMIUM FLUORIDE, CdF

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ABSTRACT. The spectrum observed by Asundi, Samuel and Zaki-uddin and attributed by them to cadmium fluoride, CdF, has been identified with the known spectrum of calcium fluoride, CaF. New experimental work with cadmium fluoride is briefly described. Mention is also made of absorption bands incorrectly attributed to cadmium bromide and cadmium iodide.

§ 1. PREVIOUS WORK ON THE SPECTRUM OF CADMIUM FLUORIDE

TWO emission band systems, in the yellow-green and orange regions of the spectrum, have been observed by Asundi, Samuel and Zaki-uddin⁽¹⁾ in an arc containing cadmium fluoride. These bands were analysed and attributed to the molecule CdF.

During the course of other investigations, we noticed that the head of the strongest sequence of the orange system was coincident with that of the calcium-fluoride spectrum, at 6064 Å. A closer investigation revealed that the two spectra were very probably identical. In table 1 the wave-lengths, intensities and analysis of the two strongest sequences of bands in the orange attributed to CdF by Asundi, Samuel and Zaki-uddin are compared with the corresponding heads in

Table 1

CdF			CaF		
λ	Intensity	v', v''	λ	Intensity	v', v''
6064.3	4	0, 0 Q_1	6064.4	10	0, 0 Q_{12}
6061.8	4	1, 1 Q_1	6062.3	9	1, 1 Q_{12}
6060.0	5	2, 2 Q_1	6060.4	8	2, 2 Q_{12}
6058.8	3	3, 3 Q_1	6058.6	7	3, 3 Q_{12}
6057.6	5	4, 4 Q_1	6057.0	6	4, 4 Q_{12}
6056.0	3	5, 5 Q_1	6055.5	5	5, 5 Q_{12}
6054.7	3	6, 6 Q_1	6054.0	5	6, 6 Q_{12}
6053.3	1	0, 0 P_2	6052.8	4	7, 7 Q_{12}
6036.9	4	0, 0 Q_2	6036.9	6	0, 0 Q_2
6034.6	3	1, 1 Q_2	6034.8	6	1, 1 Q_2
6032.5	3	2, 2 Q_2	6032.9	5	2, 2 Q_2
6031.0	2	3, 3 Q_2	6031.1	5	3, 3 Q_2
6029.3	1	4, 4 Q_2	6029.3	4	4, 4 Q_2
6027.9	1?	5, 5 Q_2	6027.8	4	5, 5 Q_2

the calcium-fluoride spectrum as measured by Johnson⁽²⁾; the wave-lengths given by the latter are only reproduced here to the nearest 0.1 Å.; the analysis is that proposed by Harvey⁽³⁾.

It will be seen that the wave-lengths agree closely; for the weaker bands the agreement is slightly less close but still quite convincing. The general intensity-distribution throughout the two systems is also in satisfactory agreement. The analysis proposed for the bands attributed to CdF is similar to the accepted analysis for CaF but differs in detail.

The agreement between the wave-lengths of the yellow-green bands reported by Asundi, Samuel and Zaki-uddin and those for calcium fluoride is not nearly so complete, but as the characteristic groups of calcium lines at $\lambda\lambda 5602.8, 5601.3, 5598.5, 5594.5, 5590.1, 5588.7, 5582.0$ and $\lambda\lambda 5270.3, 5265.5, 5264.2, 5262.3, 5261.7$ appear in the reproduction of their photograph showing the yellow-green bands, it seemed desirable to check these experimentally.*

§ 2. EXPERIMENTAL OBSERVATIONS

Using a glass prism spectrograph giving the visible spectrum on a 12 in. plate, and a Hilger E. 1 quartz spectrograph, we have photographed spectra obtained by introducing cadmium fluoride into an arc between cadmium electrodes, and calcium fluoride into an arc between graphite electrodes. An arc between graphite electrodes fed with cadmium fluoride has also been photographed in the green with a 20-ft. concave grating spectrograph giving a dispersion of 3.8 Å./mm. in the first order.

The CaF bands in the orange and yellow-green appeared on all the spectrograms of the cadmium-fluoride arcs, although the calcium lines were less intense on our plates than in the reproduction of the yellow-green bands shown by Asundi, Samuel and Zaki-uddin. Direct comparison of the spectra obtained with the fluorides of calcium and cadmium showed that there were no other bands in the yellow-green or orange that could be assigned to a fluoride of cadmium.

No strong well-developed system of bands which could be attributed to CdF appeared on our plates between 6800 Å. and 2400 Å., but a few rather weak bands were observed in the region 3000–2800 Å. The approximate wave-lengths and intensities of these are listed in table 2; the letters *R* and *V* indicate that the band is degraded to longer or shorter wave-lengths respectively.

Table 2

λ	Degraded to	Intensity
3005	<i>R</i>	5
2961.5	<i>V</i>	5
2908	<i>R</i>	2
2904	<i>R</i>	1
2862	<i>V</i>	5
2819	<i>V</i>	3

* Subsequently we discussed the identity of these spectra with Prof. Samuel, who since informs us that Dr Asundi has re-examined the plates and verified our conclusions.

We have not succeeded in identifying these bands, but in view of their rather inconsistent behaviour we hesitate to attribute them to CdF. In addition to calcium, thallium was present as an impurity in our cadmium; the spectrum of thallium fluoride⁽⁴⁾ lies in the same region as the bands listed above, but the wave-lengths of the individual bands do not agree. The emission spectra of cadmium chloride, bromide and iodide observed by Wieland⁽⁵⁾ all lie in the region 3500 to 3000 Å., and hence the bands listed in table 2 seem to be in quite a likely part of the spectrum for CdF.

§ 3. ABSORPTION BANDS ATTRIBUTED TO CADMIUM BROMIDE AND IODIDE

Walter and Barratt⁽⁶⁾, Barratt⁽⁷⁾, and Barratt and Bonar⁽⁸⁾ have studied the absorption band spectra produced by various cadmium compounds and by various impurities which occur in cadmium; various band systems observed by earlier workers and attributed to Cd₂, CdO and InCd were identified with CdCl, TlCl and Bi₂. Walter and Barratt tabulate some absorption bands which they attribute to cadmium bromide and cadmium iodide; these bands were not observed by Wieland⁽⁵⁾ in emission. We have noticed that the absorption bands attributed to cadmium bromide agree within the limits of measurement with the band system of thallium bromide observed by Butkow⁽⁹⁾ and that of those attributed to cadmium iodide some agree with bands of thallium iodide⁽⁹⁾ and the remainder with bands of bismuth iodide⁽¹⁰⁾.

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COLOUR SENSATIONS PRODUCED BY ULTRA-VIOLET LIGHT

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ABSTRACT. The crystalline lens of the author's left eye has, as the result of an accident, been destroyed. The eye is now sensitive to ultra-violet light of quite low intensity. The sensation between 3600 and 3100 Å. is blue, not violet. The sensations produced by extremely faint ultra-violet light on the dark-adapted retina are discussed; the behaviour is essentially similar to that in normal scotopic vision, the light appearing colourless and the peripheral region being more sensitive than the fovea.

§ 1. INTRODUCTION

IT has been reported by Saidman⁽¹⁾ that young people with normal sight can see ultra-violet light of high intensity as far as 3341 Å. He says there is a focused image on the retina which produces a blue sensation, and a violet halo surrounding this image due to fluorescence of the lens of the eye. The ability to see beyond about 3800 Å. is, however, lost with advancing age. It has also been recorded that people who have had an operation for cataract, involving removal of the crystalline lens, are able to see down to 3020 Å. Similar observations have been made by de Groot⁽²⁾. Nevertheless it does not seem to be common knowledge that ultra-violet light produces a blue sensation; moreover I have been unable to find a record of any observations on scotopic vision for ultra-violet light. It therefore seems desirable to record in some detail the sensations that are produced by light between 4000 and 3100 Å. now that the lens of my eye has been destroyed.

§ 2. THE HISTORY OF THE EYE

Before the accident my colour vision was quite normal. In 1933 it was tested by Mr F. H. G. Pitt at the Royal College of Science and my colour-matching and hue-discrimination were not in any way abnormal.

In January 1936, while distilling some di-iso-propyl ether* at the British Cotton Industry Research Association, I was involved in a very severe explosion. My right eye had to be removed and my left eye was badly cut by flying glass; the crystalline lens was punctured and formed a cataract. This cataract has now to a large extent absorbed. The remains of the capsule of the lens and the cuts in the cornea interfere with the sight, but by using a small stop I can obtain almost perfect definition and it seems that the retina is normal and healthy.

* Details of the explosion have been published in *Chemistry and Industry*, 55, 421 (1936).

I noticed as sight returned that dark spectacles which most people described as of neutral colour appeared to me to be violet; I have since observed that these spectacles, which are of a very common type, although absorbing fairly uniformly throughout the visible spectrum, are much more transparent to near ultra-violet light. As soon as I was able to resume spectroscopic research work I therefore examined my colour vision, and was surprised to find that I could see quite easily down to 3300 Å. with glass spectacles on, and a little farther with quartz lenses.

My colour vision between 4400 Å. and the red appears to be still fairly normal, although settings with a Nagel anomaloscope show that I am relatively less sensitive to red light, my setting being on the protanomalous side of the average, but well within the range of settings made by various normal observers.

In view of the effect of age on ultra-violet sensitivity it seems relevant to record that I am aged 26.

§ 3. OBSERVATIONS WITH LIGHT OF MODERATE INTENSITY

An iron arc has been used as a source for most of the observations; I am familiar with the wave-lengths of the principal groups of lines in the spectrum of this arc and could thus dispense with a wave-length scale. I have viewed the spectrum of the arc on several spectrographs and am able to see down to 3100 Å. even on instruments of large dispersion. Some idea of my abnormal sensitivity may be gained from the fact that I find it easier to focus and adjust the slit-width of a 20-ft. concave grating spectrograph by observing second-order 3400 Å. than by using the first-order 6800 Å.

The colour sensations produced by the iron arc spectrum as obtained in a Hilger medium quartz spectrograph (E 2) using a quartz eye-piece are listed in table 1.

Table 1

Wave-lengths (Å.)	Remarks
7000 to 4600	Normal; intensity maximum in the green
4500	Blue
4400 to 4300	Blue-violet
4200 to 3900	Violet, but much stronger than as observed previously
3800 to 3700	Very strong whitish violet. The spectrum between 3850 and 3800 Å. is very intense and is almost comparable in apparent brightness with the green maximum, the light being unbearably bright if the slit is opened to a width of about 0.1 mm. This intensity is probably largely accounted for by the strength of the iron arc spectrum in this region
3650	Strong whitish blue-violet
3600 to 3150	Strong blue
3100	Blue. There is some indication that the 3100 Å. iron triplet is a slightly more violet shade of blue, but this may be only a contrast effect due to the strong blue sensation produced by the neighbouring light
3091	Only just visible with normal slit width
3083	Invisible

I was at first of the opinion that the sensation produced by light between 3600 and 3300 Å. was a rather whiter blue than ordinary spectrum blue. I set up a small

spectrometer in such a way as to obtain two spectra of the iron arc, one above the other and relatively displaced along the spectrum. By moving the two spectra with respect to each other I was able to make a direct comparison of the colour of the ultra-violet light against the visible spectrum. Some slight difficulty was experienced because of the different focusing of the lenses for visible and ultra-violet light. The spectrum between 3300 and 3600 Å. was found to make an almost perfect colour-match with the small group of iron lines at 4530 Å., i.e. quite a true blue and apparently free from any sensation of white. The iron arc spectrum between 4600 and 4400 Å. as observed with prismatic dispersion appeared of similar intensity to that between 3600 and 3300 Å., the ultra-violet being if anything a little stronger; the iron arc of course is also rather stronger in this region as observed photographically.

Some observations have also been made after the eye has been fatigued to light of various colours. After fatiguing to red light the violet region between 4300 and 3700 Å. appears less violet and the sensation is then blue from 4700 right down to 3100 Å. If the eye is first fatigued to blue light, then the violet patch is more noticeable and appears redder. It therefore seems that the red sensation, in addition to the strong maximum around 6000 Å., has a second weak maximum around 3950 Å. and then falls to zero at about 3600 Å. The blue sensation as recorded by the retina, unlike that obtained by a normal eye with its absorbing lens as well, appears to be stimulated by light between 4800 and 3100 Å., where the limit is possibly set by the absorption of the cornea.

§ 4. DISCUSSION OF THE FOREGOING OBSERVATIONS

Several people have suggested that my sensitivity to ultra-violet light, now that the absorbing material of the lens has been destroyed, is due to fluorescence of the retina. I am of the opinion that this is not so. Firstly, the visual acuity for ultra-violet light and for light in the visible spectrum is the same, while judging by the behaviour of oiled photographic plates used for photography in the far ultra-violet, I should expect a deterioration in the visual acuity for a fluorescence effect. Secondly, the sensitivity seems to be much about the same from 4300 to 3100 Å.; since for fluorescence the light must presumably be first absorbed by some substance in the retina and then re-emitted in all directions, I should expect a relatively much lower efficiency for fluorescence than for the normal process of sight. Thirdly, the fluorescent light emitted by most, though of course not all, organic compounds consists of a rather extensive continuous or banded region of the spectrum; light of wave-lengths between 3600 and 3100 Å. seems to me to make an almost perfect colour-match with λ_{4530} , in which region only the blue sensation is stimulated at all strongly; if the sensation of light was being produced by fluorescence over a broad region of the spectrum, the saturation of the colour observed would be low and an admixture of white with the blue would be required to make a good match against the ultra-violet light. Taken individually none of the above reasons is conclusive evidence that the sensation produced by ultra-violet light is not caused by fluorescence of the retina, but taken collectively the three reasons must be considered as very strong. Moreover, since all the sensations observed for ultra-violet light are

qualitatively, and roughly quantitatively, the same as those produced by light in the visible spectrum, it seems quite unnecessary to postulate any mechanism alternative to that for ordinary sight.

It seems that it should now be possible to draw three-colour mixture curves of the type drawn by Wright and Pitt⁽³⁾ for the retina itself between 7000 and 3100 Å.; these curves will differ from those for a normal eye because the latter are modified by absorption of light by the crystalline lens, which reduces the intensity of the violet light falling on the retina and cuts off all but a very small fraction of the light below 3800 Å. Any attempt to draw these colour-mixture curves quantitatively would necessitate erecting special apparatus and calibrating light sources for the ultra-violet; this I have so far made no attempt to do. I have however sketched out the probable trend of my *sensation* curves in figure 1; the curves have been drawn from

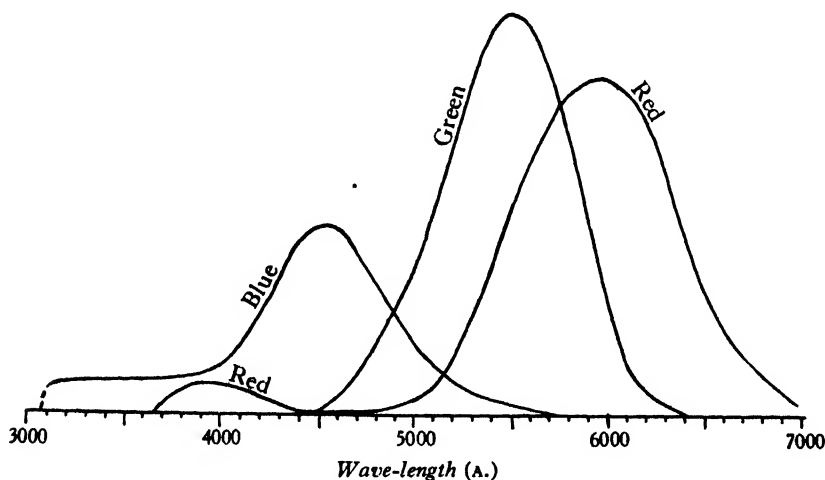


Figure 1.

visual observation of the spectrum assisted by the fatigue-experiments already described, by my photopic luminosity curve, which has been roughly measured between 4800 and 4000 Å., and by a qualitative estimate of my hue-discrimination, which shows a minimum of sensitivity around 4000 to 3900 Å., a comparatively high sensitivity around 3700 to 3650 Å., and practically zero sensitivity below 3600 Å. These sensation curves, which are of the type drawn by König and others, are of course purely qualitative, and cannot be considered as more than careful guesses. Blue light has of course a very small luminosity compared with the green, and in order to show the interesting features of the blue sensation below 4300 Å. I have had to draw the blue sensation curve to a larger scale than the others.

The colour-mixture curves published by Wright and Pitt show a rise of the red coefficient to a very flat maximum around 4200 Å. The red maximum which I observe between 4000 and 3900 Å. is quite definite, and the change in the appearance of this region of the spectrum produced by fatiguing the eye to red light is almost startling. It is difficult to compare the intensities of the sensations produced by

widely different regions of the spectrum, as no allowance can readily be made for the intensity-distribution of the light from the source, so the relative heights of the two red maxima are rather indeterminate.

§ 5. SCOTOPIC VISION

Source. For examination of the sensitivity of the dark-adapted eye to very weak ultra-violet light, a very weak source which is relatively rich in ultra-violet light is necessary. A neon lamp run through an extremely small capacity glows feebly, and as the neon spectrum has several fairly strong lines between 3800 and 3300 Å. this seemed suitable as a source. It was used in conjunction with an ultra-violet filter which transmitted between 3830 and about 3300 Å. This filter appeared almost black to people with normal sight, the filament of an electric lamp being only just visible when held right up against the filter. The neon lamp was run from the 230-volt a.-c. mains through a switch, which was turned off but to which about 4 ft. of ordinary flex was connected, the other ends of the flex being unconnected; this flex acted as a small capacity and the lamp glowed so feebly that it was barely visible in ordinary light. Some idea of the extreme weakness of this source when viewed through the ultra-violet filter may be gathered from the fact that to darken a fast photographic plate (Ilford Monarch, H. & D. 525) slightly (to an optical density of 0.2) an exposure of 2 hr. at 10 in. was necessary, equivalent to an exposure of roughly 100 hr. at the distance at which it could just be observed by the dark-adapted eye.

Observations. The process of dark-adaptation took rather long, and after half an hour in a photographic dark room it was only possible to see the lamp through the filter at a distance of 3 ft. With my eye completely dark-adapted (in the middle of the night after several hours in bed) I was just able to see the lamp at a distance of roughly 6 ft.

The sensation produced by such faint light was of course quite colourless. It was also noticed that the lamp was most easily observed by looking slightly to one side so that the image fell not on the fovea but on the outer part of the retina. This is of course also the case for scotopic vision with light of other colours, and in fact the observations for ultra-violet light and visible light seem to be in all ways at least qualitatively the same. The degree of dark-adaptation and the sensitivity of the retina to faint ultra-violet light are high.

Discussion of the observations. In view of the preliminary nature of the observations recorded above, and as I have so far not been able to measure my scotopic luminosity curve, it would be unprofitable to discuss existing theories of scotopic vision or to make any suggestions to account for the apparently high sensitivity of the dark-adapted retina to light below 3800 Å. The scotopic luminosity curve for a normal eye has a maximum in the green⁽⁴⁾ and falls off sharply on the short-wave-length side at about 4500 Å. The visible absorption band of visual purple⁽⁵⁾ agrees very closely with the scotopic luminosity curve, and photochemical bleaching of thin films of visual purple varies with wave-length in much the same way, the similarity of these three curves being in fact the basis on which visual purple is

assumed to be intimately connected with scotopic vision. Recently Dartnall and Goodeve⁽⁶⁾ have pointed out that the absorption of visual purple is higher in the violet than that indicated by a luminosity curve drawn so that the maxima of the curves coincide, and have attempted to correct the luminosity curve for absorption by yellow pigmentation of the retina and absorption of the lens. A quantitative comparison of my scotopic luminosity curve with the absorption by visual purple down to 3100 Å. would be very interesting.

§ 6. CONCLUSION

It seems that measurements of the colour-vision and scotopic-luminosity curves of subjects who have had an operation for cataract, and who are thereby sensitive to ultra-violet light, might considerably extend our knowledge of the very complex problems associated with vision, and that the region of the spectrum between 4000 and 3100 Å. would well repay a more thorough study than it has so far received.

§ 7. ACKNOWLEDGEMENTS

I should like to express my thanks to Dr R. W. B. Pearse and Dr W. D. Wright for helpful discussion, and to Miss W. M. McKeon for co-operation in measuring my photopic luminosity curve in the blue.

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DISCUSSION

Prof. ALLAN FERGUSON. I have had the lens of my left eye removed as the result of the development of a simple cataract, but I have not, as yet, made any quantitative investigations of the type described by Dr Gaydon. Qualitatively I notice that mercury-vapour lamps appear as surrounded by a vivid violet aura, and that, after a day spent in brilliant sunshine, I observe the late afternoon sky as very rich in reddish-purple hues, the psychological effect being oddly unnatural. Further, at any period, acuity of vision falls off very rapidly as darkness comes on. I cannot resist taking this opportunity to congratulate the author on the courage and pertinacity which has enabled him to obtain so much of good from a misfortune so serious.

Dr W. D. WRIGHT. This paper is of very considerable interest and should prove of value in furthering our knowledge of the visual processes. My main regret is that our colorimeter, on which the author took certain of his observations, was not

designed to extend into the ultra-violet and so did not enable him to record any quantitative observations on colour-mixture and hue-discrimination. I tried to persuade Dr Gaydon to guess his hue-discrimination curve, but could not induce him to be so rash. It would appear, however, that on the assumption that a minimum in the curve occurs where the hue is at a point of change between two main sensations, for instance at the blue-green, an extra minimum should occur at about 3800 Å., where the hue is changing back from purple to blue. The main value of the results will no doubt be found in relating them to the photo-chemical processes occurring in the retina. It would, of course, have been very exciting if Dr Gaydon had experienced a new sensation altogether in the ultra-violet.

Dr F. H. G. PITT. The author has remarked that persons who have had an operation for cataract, involving removal of the crystalline lens, are able to see down to 3020 Å. I know one who has had a cataract removed from his left eye and he, too, can see well down into the ultra-violet, and like Dr Gaydon sees this as a blue sensation. He can also see weak light-sources through an ultra-violet filter (Wratten No. 18a).

AUTHOR'S REPLY. I also have noticed the purple effect after sunset remarked on by Prof. Ferguson, the colour being particularly noticeable if seen in contrast with artificial light.

In reply to Dr Wright, I have stated in the paper that my hue-discrimination has a maximum of sensitivity (i.e. the curve shows a minimum) around 3700 or 3650 Å.; the sensitivity here is probably about 10 to 20 Å., but as the colour of the light appears to change slightly with intensity, being relatively blue for strong light and violet for light of low intensity, it is not easy to draw a quantitative hue-discrimination curve.

I am very interested to hear that Dr Pitt's friend confirms my observations.

Recent measurements made by Dr C. F. Goodeve at University College indicate that my eye, when dark-adapted, is roughly 1000 times as sensitive, compared with the green maximum, as a normal eye to light of wave-length 3650 Å. For this wave-length the sensation is blue for light of high intensity, violet for light of low intensity and colourless for very weak light.

THE DISSIPATION OF ENERGY BY A PENDULUM SWINGING IN AIR

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ABSTRACT. The decrement of a pendulum falls slowly with the amplitude: hence the need for determinations based on small changes of angle. The resulting errors of observation lead to erratic values but not to systematic error. The result of measurements with a seconds pendulum enclosed in a case is shown by a smoothed curve, the departure from observed times being expressed by *smoothing fractions*, and a *smoothing figure* is a measure of this departure for the whole or part of the experiment. From the decrement the rate of loss of energy is calculated. This 7 kg. pendulum with amplitude 53' dissipates a Board of Trade Unit (which serves a 70 w. lamp for 14 hours) in rather over 100,000 years. Experiments with different pendulums are described by which the component losses due to suspension, rod, and bob are found. Suspension springs made from thin strip clamped in chaps dissipate large and variable amounts of energy compared with springs made from thick strip ground thin in the middle. The variable losses are associated with variable rates of the pendulum. The cylindrical case adds considerably to the air resistance. The measured loss due to a gravity impulse lever is little in excess of the computed loss from collision with the pendulum: for a seconds pendulum 1/2000 part of the free pendulum loss.

§ 1. DECREMENT AND ENERGY DISSIPATION

SUPPOSE a pendulum encounters at each moment a resistance proportional to its velocity, producing an acceleration $2\delta\dot{\theta}$ radian/sec.² when the pendulum makes an angle θ with its position of rest. The equation of motion is then

$$\ddot{\theta} + 2\delta\dot{\theta} + dg\theta/K^2 = 0 \quad \dots\dots(1),$$

d being the distance of the centre of gravity below the turning point and MK^2 being the moment of inertia of the pendulum of mass M g. about this point in C.G.S. units. It follows that

$$\theta = \alpha_0 e^{-\delta t} \sin nt$$

t seconds after the moment when θ was 0 and the amplitude α had its initial value α_0 , amplitude being the semi-arc, and

$$n = \sqrt{\frac{dg}{K^2}} = 2\pi \text{ times the frequency of oscillation.}$$

Thus $\alpha = \alpha_0 e^{-\delta t}$ and δ is found from t_1 and t_2 for α_1 and α_2 respectively from

$$\delta = (\log_e \alpha_1 - \log_e \alpha_2) / (t_2 - t_1) \quad \dots\dots(2).$$

I call δ the *decrement*.* Then,

$$\delta = -\frac{1}{\alpha} \frac{d\alpha}{dt}$$

$$\text{i.e.} = -\frac{\Delta\alpha}{\alpha} \text{ per second.}$$

Logarithmic decrement is defined as $-\Delta\alpha/\alpha$ per cycle and is equal to $2\pi\delta/n$.

The energy of the pendulum $= \frac{1}{2}MK^2n^2\alpha^2$,

hence the loss of energy

$$= MK^2n^2\alpha\Delta\alpha$$

$$= 2\pi n\delta MK^2\alpha^2 \text{ erg/c.} \quad \dots\dots(3).$$

§ 2. OBSERVATIONS FOR DECREMENT

The decrement in an electrical circuit consisting of a condenser in series with an air-cored inductance is independent of the current-amplitude, provided Ohm's law holds good. With a pendulum, on the other hand, δ decreases slowly with α and must be determined by observations of t for successive values of α differing, say, by 2.5'. In an investigation of the relation between rate and arc⁽¹⁾ δ was needed for calculating the effect of maintenance. Comments which I made on these measurements did not, apparently, distinguish clearly between erratic values and systematic error.† I will, therefore, describe an observation.

The micrometer eyepiece is adjusted so that a line on the moving scale fixed to the pendulum comes to rest beyond the index, whilst another line travels to an equal distance beyond it at the other end of the swing. As the amplitude falls these stationary positions approach the index, and the moment is recorded when a line appears to coincide with the index, the other line doing so half a cycle later.

An error of observation consists in ante-dating or post-dating the event, i.e. in recording a moment when the lines do not coincide with the index.

§ 3. EFFECT OF ERRORS OF OBSERVATION. SCALE-CALIBRATION

In table 1 α becomes 82.14' (column 1), 1275 sec. (column 6) from the start. Suppose the true time is 1272. The error has made the preceding interval 446 sec. instead of 443 (making $10^7 \delta$ too small by 4.6 units) and the succeeding interval 454 instead of 457 (making $10^7 \delta$ too large by 4.4 units). The error makes a difference of 9 units in the drop from one value of δ to the next, but its effect on the average value is quite inappreciable, i.e. it does not introduce systematic error.

The angular errors in estimating coincidences of lines with index are probably about the same for all amplitudes; possibly better observations are obtained with large amplitudes when the glimpse of the line in its stationary position is more

* In a previous paper⁽¹⁾ I described δ as logarithmic decrement in error.

† Prof. R. A. Sampson⁽²⁾ supposed that the values used might be systematically too large by 10 per cent or even by 24 per cent.

Table 1. Decrement of E_{14} in cylindrical case. (Barometer 540 mm.)

1	2	3	4	5	6	7	8	9	10	11	12
α	$\Delta \log_e \alpha$	Seconds observed				δ_{10} $\times 10^7$	δ smoothed $\times 10^7$	Seconds calc	Seconds calc. - obs.	Smooth- ing fraction $\times 10^4$	Square $\times 10^4$
		Oct.	Nov	Mean	Total						
89.60									+3	75	56
87.15	0.02768	396	412	404		687	690	402	+1	25	06
84.62	0.02932	430	421	425	404	681	685	427	+3	69	48
82.14	0.02992	446	446	446	829	675	679	440	-3	66	44
79.65	0.03088	456	451	454	1,275	666	672	460	+3	64	41
77.15	0.03184	481	483	482	1,729	658	663	480	+1	20	04
74.65	0.03289	501	510	505	2,211	648	654	502	-2	39	15
72.13	0.03441	531	533	532	2,716	640	645	534	0	0	0
69.64	0.03508	546	546	551	3,248	631	636	552	+1	17	03
67.15	0.03640	574	586	580	3,799	627	627	581	+2	33	11
64.62	0.03846	630	625	628	4,379	615	619	622	-4	63	40
62.14	0.03907	651	637	644	5,007	612	615	646	-2	31	09
59.69	0.04022	647	659	653	5,651	610	612	658	+3	45	20
57.26	0.04166	685	681	683	6,304	605	608	685	+5	70	49
54.76	0.04461	740	737	739	6,987	597	604	739	+5	66	43
52.27	0.04654	789	782	785	7,726	592	598	780	0	0	0
49.79	0.04863	834	834	834	8,511	581	589	825	-9	104	108
47.27	0.05190	881	876	879	9,345	573	580	895	+7	75	56
44.77	0.05436	964	976	970	10,224	568	570	954	-9	90	81
42.24	0.05817	1047	1,031	1039	11,194	562	562	1033	-15	141	199
39.74	0.06106	1073	1,080	1076	12,233	558	558	1093	+2	19	04
37.28	0.06388	1134	1,143	1139	13,309	552	554	1152	+15	125	157
34.81	0.06858	1269	1,264	1266	14,448	545	549	1250	-1	08	01
32.32	0.07416	1375	1,364	1370	15,714	538	543	1364	-7	49	24
29.85	0.07950	1503	1,464	1483	17,084	535	537	1481	-9	57	33
27.37	0.08663	1638	1,610	1624	18,567		531	1631	-2	10	01
16.99	0.04770		8,940		20,191		(534)				
4.87	1.250		24,300				(515)				1053

Smoothing figures: $\sqrt{(1053 \times 10^{-6}/26)}$, equal to 0.00637 for whole series; $\sqrt{(605 \times 10^{-6}/6)}$, equal to 0.01005 for 50' to 35'; $\sqrt{(448 \times 10^{-6}/20)}$, equal to 0.00473 for remainder. October times have been increased 1.1 per cent to correct for higher pressure. First and last figures in column 7 relate to 5' intervals.

momentary. Thus the fraction (error in seconds/interval for 2.5') measures the proportional error in δ and also, being proportional to the angular error, may be taken as a measure of the unreliableness of observation.

Unequal spacing of scale divisions is another source of error. The scale used with pendulum E since 1931 was ruled on ivory by a firm of opticians to replace my amateur effort, yet in this the largest space exceeds the smallest by 4 per cent. I have recently recalibrated it, using the micrometer eyepiece arranged to give a magnification such that 500 divisions on the micrometer head correspond to the 2.5' space.

§ 4. DECREMENT-DETERMINATIONS IN 1934 AND 1937

The δ values already referred to were obtained in 1934 from two runs, but for half the intervals observations from one run only were available. From such meagre material, a spread of points on the graph was to be expected, but two

especially low points near $50'$, not balanced by high points on either side, suggested that some resonant effect due to the cylindrical case might exist for this angle.

In October and November 1937 I made observations with pendulum E_{14} (similar to E_{11} but for a larger bob for which $M=7.2$ kg. as compared with 6.2 for E_{11}) in the same enclosure. Two runs were used from each month. Between the experiments, I made two changes in the micrometer which experience shows to have improved the observing, but I have assigned equal weight to October and November.

Table 1 will make clear the way in which I have used this material. Values for δ are calculated from time intervals for $10'$, e.g. from $89.60'$ to $79.65'$ and next from $87.15'$ to $77.15'$; all amplitudes are corrected by calibration and reduced to true minutes of arc (column 7). These values have been used as a guide to obtain smoothed values (column 8), for the original $2.5'$ intervals. With any smoothed value there is associated a time interval derived from equation (2) which is entered in column 9, and from this column 10 is built step by step giving a calculated time for reaching each angle and thence the difference between calculated and observed times. For example, $\alpha=64.62$ is entered as being reached 5007 seconds from the start. The calculated time is 5003 (assuming that 89.60 occurred 3 seconds later than recorded). The smoothing process consists in reconciling so far as possible regularity in change of δ with agreement between computed and observed times. It should be remembered that an observation is not an interval of time but the start or finish of such, and column 10 shows to what extent an arbitrary manipulation of figures involves departure from the observed times. The *smoothing fraction* in the above case $= -4/\{(622+646)/2\} = 0.0063$ (cf. § 3). The root mean square of a series of such fractions may be called the *smoothing figure* for the series, and its smallness is an indication of the confidence which may be placed in the result.

§ 5. THE DECREMENT CURVE

The 1937 result is shown on a large scale (for the zero line is far below the figure in A of figure 1. The smoothing figure is 0.0064 (the factors at the heads of columns 7, 8, 11 and 12 of table 1 should be noticed), as compared with 0.0118 for the 1934 curve obtained in the same way. If we bear in mind the time and care expended to obtain the later results compared with the earlier, the smaller smoothing figure is not surprising.

It will be noticed in column 11 that the smoothing fraction reaches 0.01 in three cases, all of them in the region $\alpha=50'$ to $35'$. For this region the smoothing figure is 0.0100 , and it is 0.0046 for the rest of the curve. On comparing the October figures with those obtained in November, I find that the irregularities of δ in this region are strikingly similar in the two cases. This would result from faulty calibration of the scale, but the deviations are five times as large as any that can come about in this way since the latest calibration.

I think that the curve represents the truth fairly closely, but it may have been simplified too much between $50'$ and $30'$. It lends no support to the 1934 observations of low values around $50'$. The hump between 45 and 65 is real. I suppose the

shape of the curve is largely due to the 20 cm. cylindrical case: I cannot see how the two regions of relatively low values would occur with a pendulum swinging in the open.

Study of these large-scale curves tends to give an exaggerated idea both of the amount and of the irregularity of change of δ . I have therefore added curve *B*, which is the same as *A* but on a smaller scale so that the zero line also appears.

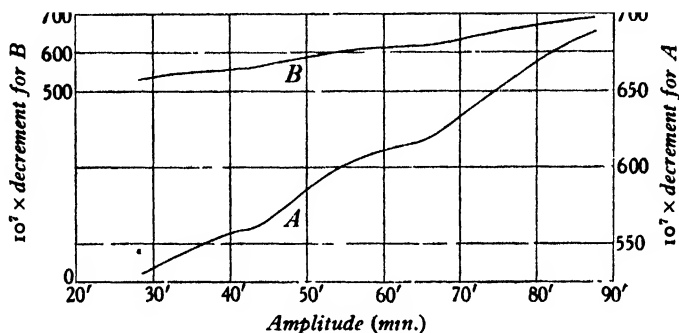


Figure 1. Decrement of seconds pendulum E_{14} in cylindrical case at 540 mm.

§ 6. ENERGY-DISSIPATION. CHANGES IN δ

The loss of energy at any amplitude can be obtained from equation (3) when the moment of inertia (6.9×10^7 g.-cm.² for E_{14}) is known.

Taking $\alpha = 53'$, for example, table 1 gives $\delta = 596 \times 10^7$, $n = \pi$ (seconds pendulum). The loss $= 2\pi^2 \times 596 \times 6.9 (53/3438)^2 = 19.3$ erg/c. This loss (9.6 ergs per second) may sound a large amount, and it is enormous compared with the flow of energy needed for radio reception. On the other hand, a Board of Trade Unit (which serves a 70 watt lamp for 14 hours) is 3.6×10^{13} ergs, so that the pendulum loses this amount of energy in 118,000 years.

When a pendulum is maintained at a steady amplitude, the input, of course, balances the loss. When the supply is (1) very steady as it is with my gravity impulse and is (2) independent of amplitude, change in δ due to change in air-density, for example, can be measured indirectly without disturbing the clock, by noting the change of amplitude, for in this case the loss remains constant; hence

$$\frac{\Delta \delta}{\delta} + \frac{2\Delta \alpha}{\alpha} = 0 \quad \dots\dots(4).$$

I find that when air pressure is changed from 532 mm. to 586 mm., α falls from $68.49'$ to $66.91'$. From table 1, $10^7 \delta = 627$ at $68.4'$ and falls $8 \times 1.58/2.5 = 5$ with amplitude. With increased pressure $10^7 \Delta \delta = 627 \times 2 \times 1.58/68.4 = 29$, equation (4). Thus the new $10^7 \delta$ is $627 + 29$ at $66.91'$ and $627 + 29 + 5$ at $68.49'$, an increase of 34 for 54 mm., just 1 per cent per cm.

The gravity impulse fulfils the second condition that supply is independent of amplitude. Where inertia of the impulsing mechanism plays a part, the energy supplied falls off with amplitude. This happens with a Graham escapement in the

early part of the impulse. In the Shortt clock the important part of the impulse—the last part—falls rapidly with increasing amplitude. This aids in restoring a disturbed amplitude and also counteracts circular error to some extent when the impulse is timed so that it finishes after the pendulum has passed the central position.

§ 7. THE DISSIPATION COMPONENTS

The loss of energy is made up of four components due to: (a) air resistance to the bob, (b) air resistance to the rod, (c) bending of the suspension spring and (d) movement of the support. Without knowing these separate components, I realized in 1931 that I could not use data relating to a seconds pendulum (S) to predict the loss and decrement of a half-second pendulum (H) made with the same bob and spring and a shortened rod. Conversely, the components can be measured by experimenting with different pendulums and combining the results.

The decrement experiment of 1937 aimed at obtaining accurate results. On the other hand, experiments now to be described could be repeated more accurately, some data not obtained at the time (1932) have been supplied as far as possible by more recent experience, and, in one particular, uncertainty could have been removed by modifying the experiment. Moreover, the theory is approximate only, but the experiments seem to justify its use. However, results follow which are fairly accurate, and which, so far as I know, have not been obtained by other means.

§ 8. EXPERIMENTS TO MEASURE COMPONENTS

The loss per cycle is found by decrement experiments for several pendulums all supported by the same brackets through the same suspension spring D . All rods are of the same diameter ($\frac{5}{16}$ in.) and S and H have the same bob. For all pendulums the loss is found for $\alpha = 53'$ and also for S at $\alpha = 26.5'$.

Besides S and H , bobless pendulums were used consisting of rods of different lengths attached to the spring. The experiments do not distinguish between (c) and (d), and their combined effect is called *suspension loss*.

Six rod pendulums ranging in length from 90 to 15 cm. were experimented with (§ 9) and the constant suspension loss (§ 13) was separated from the variable air resistance loss which depends on length and frequency. From these results, the rod losses for S and H are obtained, and thus the sum of the suspension and bob losses is found for S and H . The former is nearly the same for the two (by compensating for the reduced rod-weight of H it would be made the same, § 13), whilst the bob loss for S is 10.0 times that for H . In actual fact the theory is not quite so simple as this, hence the need for allowing for the S loss at $26.5'$ (§ 10). The separation of bob loss from suspension loss is reduced to solving simultaneous equations.

§ 9. EXPERIMENTS WITH ROD PENDULUMS

To find how the observed losses E of the different rods are related to one another and to the rod losses of S and H , the hypothesis of § 1 is extended to the supposition that each cm. of rod meets with a resistance proportional to its linear

Table 2. Losses by rod pendulums. Rod losses by S and H

Rod	1	2	3	4	5	6	7	8
L (cm.)	90.5	70.0	49.9	34.7	24.7	15.1	43.0	I.L. in action
M (g.)	353.5	273.2	194.9	135.5	96.7	59.4	168	
n (computed, § 20)	4.10	4.72	5.75	7.27	9.34	13.79	6.31	
n (observed)	4.07	4.72	5.77	7.30	9.40	13.80	6.32	
Seconds 70/30	1021	981	902	800	622	377	893	855
$\delta \times 10^4$	8.41	8.66	9.42	10.62	13.66	22.5	Diff.	0.42
$MK^2 \times 10^{-3}$	994	463	172	60	23.0	6.52	111	
Erg/c. ($\alpha = 53'$)	5.025	2.824	1.397	0.692	0.441	0.303	I.L. loss 0.045	
Air loss/c. (suspension = 0.182)	4.84	2.64	1.21	0.510	0.259	0.121	(See § 22)	
$[(L + 0.9)^3 + 1850]$ $\times 10^{-5}$	7.65	3.58	1.33	0.470	0.186	0.0594		
κ	740	402	182.1	81.5	41.6	19.5	}	
$\sigma \times 10^5$	655	657	667	626	622	621		

$$S \quad \alpha = 53', \quad \kappa = 603.8, \quad \text{therefore } \sigma = 656. \quad \text{Rod loss} = 3.96 \text{ erg/c.}$$

$$H \quad \quad \quad 26.5 \quad 151.0 \quad \quad \quad 644$$

$$\quad \quad \quad 53 \quad 15.31 \quad \quad \quad 621 \quad \quad \quad 0.97$$

$$\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad 0.095$$

velocity. A rod-length L cm. starts at 0.9 cm. from the turning point and the air-resistance loss takes the form $\sigma n \alpha^2 \left[x^3 \right]_{0.9}^{L+0.9}$ erg/c. A platform at 15.4 cm. carries the scale. As these move in their own plane, I reckon the resistance as half that for an equal surface of rod. If s is the suspension loss for the mean angle $53'$ (§ 12),

$$E - s = \sigma n [(L + 0.9)^3 + 1850] (53/3438)^2$$

$$= \sigma \kappa \text{ erg/c.} \quad \dots\dots(5),$$

where 1850 is the platform term. σ , like δ , grows slowly with speed and so with κ . Each point on A figure 2 represents E for a rod (ordinate), with κ as abscissa. The graph through these points extended to the y axis will cut this in C at height s erg/c. The line A is supposed to be the tangent at C to the graph, passing very nearly through points 6 and 5. Line B represents the lower end of A on a ten-fold scale, and shows that the constant (§ 13) s is about 0.18 erg/c. The value 0.182 is found by trial so as to make σ for rod 6 just less than σ for rod 5.

Equation (5) shows that if the line joining C to 3 (say) makes angle θ_3 with the horizontal, then $\sigma_3 \times 10^2 = \tan \theta_3$ (account being taken of the scales used for the co-ordinates). Thus, the fact that the points for the longer rods stand above the line which passes nearly through 5 and 6 indicates that σ grows with κ .

The three arrows show values of κ for H and the two cases of S for which we need to know the resistance (in calculating κ for these, there is no platform term).

κ ranges from 20 to 740, and the comparatively small change in $10^5 \sigma$ from 620 to 660 suggests that the values chosen for S and H will not be far wrong. The worst determination of E appears to be the one for rod 3.

The observed results and calculations are shown in table 2. Columns 7 and 8 refer to impulse lever losses (§ 22). The computed value of n (§ 20) is not used in

finding the losses. "Seconds 70/30" means the time interval between $\alpha=70$ scale divisions and $\alpha=30$. The relation between this range and 53' is discussed in § 12.

All experiments were made in the open air. Records were made of pressure and temperature, but no corrections were applied for the small changes. M is the weight of the rod. In addition there is 5 g. at 15.4 cm. for platform and scale. For S and H the values of κ are calculated and these give the appropriate values of σ and, finally, the air resistance for the rods is $\sigma\kappa$.

The suspension loss 0.182 erg/c. is an interesting quantity (§ 21). It relates to light pendulums only and must not be confused with the much heavier loss with S and H .

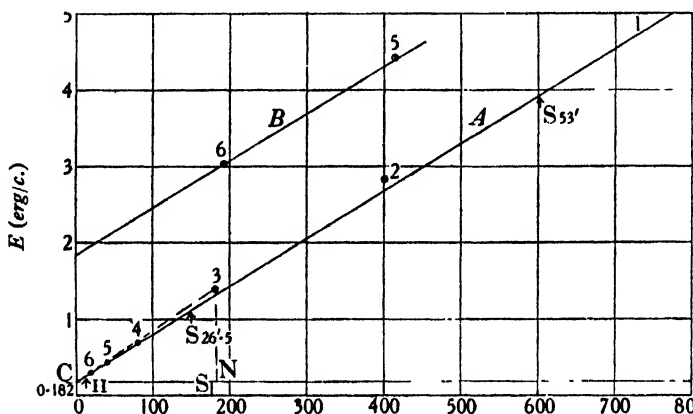


Figure 2. Loss of energy by rod pendulums. In open at 750 mm.

§ 10. CALCULATION OF COMPONENTS FOR S AND H

To find the ratio of the bob losses, the same principle is applied as before. If the flat ends of the cylindrical bob are at L_1 and L_2 cm. from the turning point, the resistance to the curved surface produces a loss which may be written

$$3\sigma\alpha^2 \int_{L_1}^{L_2} x^2 dx.$$

The surface πr^2 of each end has the same area as $\frac{1}{2}\pi r$ cm. of the curved surface, but as these ends move in their own planes σ is reduced to $\rho\sigma$, say where $1 > \rho > 0$, so the whole loss is

$$3\sigma\alpha^2 \left[\int_{L_1}^{L_2} x^2 dx + \rho r (L_1^2 + L_2^2)/2 \right].$$

Using σ for S and σ' for H and inserting the numerical values of L_1 , L_2 and r , we have

$$\frac{H \text{ bob loss}}{S \text{ bob loss}} = \frac{\sigma}{\sigma'} \frac{4970 + 1186\rho}{580 + 148.5\rho}.$$

The coefficient of $\sigma/\sigma' > 8.45$ ($\rho=1$) < 8.57 ($\rho=0$). For want of better knowledge, I put $\frac{1}{2}$ for ρ as in § 9 and then the ratio is $8.50 \sigma/\sigma'$.

With its longer rod S is heavier than H and the suspension loss is greater for S than H by an unknown amount. If this is y erg/c. for H , I give one solution for the case in which the S loss is $1.04y$ and another for $1.08y$ (§ 13). The bob loss for H being x erg/c., that for S at same amplitude ($53'$) is $8.50x \times \sigma/\sigma'$. It would, therefore, be just $8.50x$ if the change in σ due to the change in range of velocities were neglected. Now, S with α equal to $26.5'$ has the same range of bob velocities (strictly for mid-bob only) as H has at $53'$, and the transition to S at $53'$ neglecting change in σ is in the ratio of squares of linear amplitudes, i.e. $4:1$.

Table 3 shows the steps in calculation. Total losses are observed quantities, rod losses come from § 9, and suspension losses are expressed as above in terms of y ; $1.04y/4$ for S $26.5'$ assumes that the loss $\propto \alpha^2$. This should be true for bracketing and it is so for an unloaded spring. I think that it is probably not exactly true for a spring supporting a heavy pendulum. Bob losses expressed as remainders contain y and they can also be expressed in terms of x according to reasoning which I have just given (and which is not perhaps self-evident at first sight). Hence values for x , y and σ/σ' .

Table 3. Components of loss for S and H (ergs per cycle)

Amplitude	Suspension loss for $S=$					
	(1) $1.04y$			(2) $1.08y$		
	H $53'$	S $53'$	S $26.5'$	H $53'$	S $53'$	S $26.5'$
Total loss	2.658	19.37	4.257		As in (
Rod	0.095	3.96	0.97		As in (
Suspension	y	$1.04y$	$1.04y/4$	y	$1.08y$	$1.08y/4$
Bob	$\begin{cases} 2.563 \\ -y \\ x \end{cases}$	$\begin{cases} 15.41 \\ -1.04y \\ 8.5x\sigma/\sigma' \end{cases}$	$\begin{cases} 3.305 \\ -1.04y/4 \\ 8.5x/4 \end{cases}$	$\begin{cases} 2.563 \\ -y \\ x \end{cases}$	$\begin{cases} 15.41 \\ -1.08y \\ 8.5x\sigma/\sigma' \end{cases}$	$\begin{cases} 3.305 \\ -1.08y/4 \\ 8.5x/4 \end{cases}$
	$x = 1.415, y = 1.148, 8.5\sigma/\sigma' = 10.05$			$x = 1.408, y = 1.155,$		

Results

Amplitude	(1) $1.04y$			(2) $1.08y$		
	H $53'$	S $53'$	S $26.5'$	H $53'$	S $53'$	S $26.5'$
Bob	1.41	14.22	3.01	1.41	14.16	3.00
Rod	0.09	3.96	0.97	0.09	3.96	0.97
Suspension	1.15	1.19	0.30	1.15	1.25	0.31
Impulse	0.04	0.01 to 0.02	—	0.04	0.01 to 0.02	—
	2.69	19.38	4.28	2.69	19.38	4.28

Bob dimensions: 16.5 cm. long \times 7.8 cm. in diameter. Rod 0.79 cm. in diameter. Pendulums swinging in open air at about 750 mm.

The second part of the table gives final results. For solving the equations I have worked to three places of decimals, but the experimental work does not justify the retention of more than two. I have added impulse lever losses (§ 22) for completeness.

§ 11. VALUES OF THE COMPONENTS

I repeat that these values relate to pendulums swinging in the open air at atmospheric pressure. Bob losses are higher (§ 23) when the pendulums are inside cases. Perfect suspension would not materially reduce the spring and bracketing losses (§§ 13, 21).

Faulty design of the experiments is unfortunate, but comparison of the two solutions shows that the uncertainty introduced thereby is not very serious.

Whilst with S suspension loss forms about 6 per cent of the whole, it amounts to 43 per cent with H . W. H. Shortt⁽³⁾ in 1928 estimated the spring loss at 2 to 4 erg/c. He does not say how this figure was obtained, but it seems far too large for the suspension spring of the master pendulum.

In H , 2 cm. of rod projecting beyond the bottom of the bob adds needlessly to the rod resistance.

For equal speeds a square centimetre of rod dissipates just about twice as much energy as an equal area of bob.

Nearly $\frac{3}{4}$ of the energy lost by S is due to the bob. When low losses are desired, reductions can be made by working in low pressures and also by replacing air by hydrogen.

The size and shape of the bob, too, affects the resistance. At the amplitudes used for precision clocks the air movement is not turbulent, and the important element affecting resistance is skin friction. In such a case shape is of less importance than surface area. The bob used in these experiments is not ideal in this respect. It is made of a bronze of density 8.7, as compared with 11.4 for lead. Its height is 2.1 times its diameter, whereas the right circular cylinder of least surface for given volume has its height equal to its diameter. Actually, the difference is remarkably small— $5\frac{1}{2}$ per cent.

Some ten years ago A. W. Hirst experimented at Bristol on a pendulum fitted first with a long bob of circular section, and later with one of elliptical section having the major axis about three times the minor. Results were published by Prof. David Robertson.⁽⁴⁾ Air pressures ranged from 250 mm. to 1275 and amplitudes from 100' to 300'. With these large arcs turbulent motion is present and the oval bob has the advantage, especially with high pressures and the larger arcs. With small angles, however, the oval bob is at a disadvantage owing to its larger surface and the circular cylinder encounters the smaller resistance.

I did not realize in 1932 the need for the value of E for S at half amplitude. This I have supplied by using the ratio of decrements obtained from table 1.

§ 12. RHEINBERG SCALE AND THE MEAN ANGLE

The observations with rod pendulums and for H were made by means of a Rheinberg scale with 0.1 mm. spaces. At a distance of 15 cm. from the turning point this space subtends an arc of $2.292'$ representing amplitude $1.146'$. The scale is a photographic negative with transparent lines on a dark ground. A beam of light is reflected by mirrors through the scale to the micrometer eyepiece. This scheme proved valuable in finding the short intervals of time with accuracy. Instead of

observing coincidences with the index (§ 2), the overlapping lines only are observed. These produce a characteristic flicker after true coincidence. When this ceases the dark space between them appears quite suddenly, so that I think the moment at which the edges of the lines just touch can be observed to the nearest second. I estimate that the allowance for reading on the edge of the line is 0.1'. Thus, "70 divisions" means that $\alpha = 69.9 \times 1.146$ arc minutes.

δ , then, is found from the interval between $\alpha = 80.1$ and 34.3 , and equation 3 is true for the α for which this is the decrement. In 1932 I was satisfied to take $57'$, the average angle, but δ is a mean with regard to *time* (and not *amplitude*) and the correct amplitude depends on the shape of the δ graph.

In 1932, readings were taken for each 5 divisions fall of α and I have combined all the observations to find this shape, which is definitely steepest in the middle, easing off at each end: a result which clearly gives no true information about changes in δ and shows that the Rheinberg scale needs calibrating. As this cannot be done whilst the scale is in use, I have adopted the angle $53'$ which would be right if the graph were straight.

These half-second pendulums with heavy bobs are stumpy in appearance, since the bobs are longer than the exposed parts of the rods.

§ 13. SUSPENSION LOSSES

The combined loss due to strain of the bracketing, and bending of the spring could be found by measurements made with the pendulum in vacuo, for then these are the only losses remaining. Unfortunately for this method, the air resistance does not become negligible until the pressure has fallen far below what I could reach or measure. Air viscosity remains practically constant, whilst pressure is reduced from 760 mm. to 1 mm. Referring to experiments with a light half-second pendulum mounted on knife edges, A. L. Loomis wrote in 1933 that "the decrement was cut in half by reducing the gas pressure from 0.025 mm. to 0.001 mm." What fraction of the total loss is still due to air resistance even at 0.001 mm.?

My experiments do not distinguish between bracketing and spring losses, although it seems clear (see below and § 21) that the first is negligible for the light pendulums. When a pendulum is supported on a wooden case, as in a grandfather clock, the bracketing loss is frequently much larger than all the others combined. For a precision clock a sturdy support is important. The experiments were made on brackets attached to a 14 in. house wall. Brickwork was removed and replaced by 2 cwt. of concrete well keyed to the bricks (a tedious job). Long bolts, fixed at the back to an iron plate, were buried in the concrete and care was taken to make a rigid structure of special brackets, the top plate of the case and the *L* girder for carrying the suspension spring.

The experiments show that suspension loss increases from 0.18 erg/c. for the lightest rod (59 g.) to about 1.2 for the heaviest pendulum (7290 g.).

The bracketing part of this increases as the square of the maximum horizontal stress and so, for constant amplitude, as the square of the pendulum weight. Thus, if 1.2 ergs were entirely bracketing loss, this would correspond to 0.004 erg for the

heaviest rod and I conclude that the suspension loss for the rods is practically pure spring loss, which is very nearly the same for all the rods (§ 21).

Owing to its longer rod, *S* is 300 g. heavier than *H* (6990 g.). This increases the bracketing loss by 8.7 per cent and the spring loss to an unknown (probably very small) extent. Thus the first solution in table 3 supposes the suspension loss shared fairly equally between brackets and spring, and the second assumes that the brackets are responsible for nearly all the loss (which I regard as improbable). All ambiguity could have been avoided by adding a piece of bob to *H* which would be replaced by another on *S* of the same size and shape but 300 g. lighter.

It would be very interesting to know the value of the spring loss alone. Four years ago A. L. Loomis was studying this matter and succeeded in observing the motion of the support with an interferometer. I do not know that he has published any results.

The term *bracketing loss* is intended, of course, to include losses in walls (or pillars) and beyond.

§ 14. THE GROUND SPRING

I have asserted that the suspension losses shown in table 3 could not be much reduced and have described precautions taken to keep the bracketing part small. The suspension spring used in the experiments was first tried in 1931. This trial ended a disappointing stage in the search for precision time-keeping. I had been troubled with a pendulum which would not hold its rate. One part after another was replaced but still both rate and amplitude increased with time. Experiments in 1931 showed clearly that changes in the spring could produce such results (§ 16) and I consulted Dr A. A. Griffith, who reported that he had experienced similar behaviour in springs used for other purposes and recommended the formation of a spring by grinding away the central part from a strip of thick metal, leaving the thick ends for gripping. In this way, hardening of the metal by the cold working, where a thin strip is clamped in chaps, is avoided. This steel spring was the first one which I made in this way. More details are given later; it will suffice for the moment to say that it proved a success and was soon replaced by a ground elinvar spring (which is still in use on pendulum *E*) and so left free for the experiments I have described.

Ground springs are not a new feature in pendulum building. Keelhoff⁽⁶⁾ in 1906 takes it for granted that such springs will be used for "pendules d'observation"—by which he means those used when one seeks the greatest precision, regardless of cost. Shortt adopted them in 1921 for suspending the master pendulums of his clocks. I have recently measured one at Langleybury Church, Herts, on a turret clock built in 1879.

§ 15. CLAMPED SPRINGS

In 1923 I made a light pendulum for a grandfather clock which led to an unexpected improvement in time-keeping, mainly because it was supported by the wall instead of the clock case⁽⁵⁾. The regulation is done by weights placed on a shelf

midway up the pendulum rod in the usual way. A record of the weights used* shows that there has been no secular change in rate during 14 years although this rate is erratic. The suspension spring consists of a strip of thin invar (such was my ignorance) gripped in chaps. Its good behaviour in supporting the light (1.4 kg.) bob did not prepare me for difficulties with 7 kg. pendulums.

When I found these heavier pendulums accelerating in rate, I suspected the springs of an increase of elasticity over the whole length. To account for the changes observed in this way, so large a change in ϵ would be needed that I was told fracture must follow in a few million vibrations and I sought elsewhere for a cause. (Cf. the local hardening referred to above).

In 1931 I tried the effect of gently annealing an elinvar spring with astonishing results. The impulse which had kept α at about 38' now only sufficed for 25', but in only 18 hours matters had much improved. Further annealing showed that the bending of the metal involved heavy losses of energy and that the cold working due to the running of the pendulum rapidly hardened the elinvar.

Then I made a steel spring of 0.019 cm. strip clamped in chaps and took numerous observations for 6 weeks on a pendulum supported by it, both by taking rough decrement measures and also by making amplitude observations (§ 6) which gave more exact information. Changes in rate were observed at the same time. The amplitude was still growing at the end of the 6 weeks when the clamped spring was replaced by the ground one.

§ 16. LOSSES WITH CLAMPED SPRINGS

Table 4 shows how the decreasing loss in this clamped spring has been compared with the loss in the ground spring. I have supposed that the suspension loss (table 3) is entirely due to the ground spring: if it is partly due to bracketing, the contrast between the springs is greater still. In passing from 53' to 36' and back I have assumed that the loss $\propto \alpha^2$, which is probably not strictly true (§ 10). The first two amplitudes were observed when the pendulum was in the open, the rest with it

Table 4. Clamped and ground steel springs

Seconds pendulum. Energy loss in ergs per cycle. The maintenance supplies 11.1 erg/c.

1931	Spring	Barometer (in.)	α with 11.1 erg	Ergs with $\alpha = 36'$	Suspension loss	
					36'	53'
Mar. 22	Clamped steel	29.57	33.53'	12.8 in open	4.5	9.8
April 2		(29.21)	35.17'	11.6 in open	3.3	7.2
7		23.95	33.80'	12.6 in case	3.15	6.8
27		23.95	34.62'	12.0 in case	2.55	5.5
May 1	Ground steel (d)	(23.52)	38.60'	10.0 in case	0.55	1.2 from table 3

When pressure is in brackets, the observed α has been reduced to that for the pressure shown in the line above.

in the case. The argument proceeds *upwards*: 1.2 erg/c. at 53' (table 3) for the ground spring $\equiv 0.55$ at 36' out of a total of 10.0 with barometer at 23.95". The amplitude was read at 23.52" but this figure has been enclosed in brackets to indicate that 38.60' is the amplitude corresponding to 23.95" obtained by applying a correction for 0.43" to the observed reading. Thus 11.1 erg/c. maintains α at 38.60. The loss 10.0 for $\alpha = 36'$ is obtained by neglecting any change in δ for the small change of α , so that ergs vary simply as α^2 .

Similarly, on April 27 the loss with the clamped spring would have been 12.0 at 36', i.e. 2.0 more than with the ground spring, and this change is due solely to the spring: 0.55 erg/c. for the ground spring changes to 2.55 for the clamped one. The result for April 7 is obtained in the same way.

On April 2, the air losses are different and I have assumed that from April 2 to April 7 the spring loss fell off at the same rate as during the next period—hence 3.3 for April 2. The next step backwards is from 11.6 to 12.8 calculated as before, an increase again due solely to the spring.

At the start, then, the loss in the clamped spring is 8 times that of the ground spring. After 5 weeks the loss is only 56 per cent of its initial value.

The decrease in loss of energy was accompanied by a rapid increase in clock rate; towards the end of the 5 weeks it still amounted to 0.01 sec./day².

The annealed elinvar spring when started up showed a loss which would have been about 30 erg/c. at 53' and as has already been stated a large part of the rate of loss had disappeared after the pendulum had been swinging for 18 hours.

With ground springs, on the other hand, the amplitude remained unchanged from the first day of use and there was corresponding stability of rate.

§ 17. THE UNIFORM SPRING

The theory of the suspension spring has been dealt with by various writers^(6,7,8). About its behaviour when in use, on the other hand, I have found very little.

With a uniform spring the top end is the troublesome part, because curvature increases rapidly from the middle to the top, especially with springs which are otherwise of suitable dimensions for a precision pendulum. This is shown in figure 3 relating to springs of which details are given in table 5. The first of these is the uniform counterpart of the 1931 ground-steel spring (so far as it can correspond to a non-uniform spring). The thickness (nearly 0.006") is reasonable and the spring is certainly not too short. Its shape in use is shown as curve *A* where the amplitude is pictured as about 33° (!). Notice how nearly straight the bottom half of the spring remains and how much of the bend is taken at the top. This is shown more clearly by curve *B* which shows the curvature for all parts. The greatest curvature, 0.048, at the top falls to half value at 0.2 of the way down and to one-tenth at the lower end—the values relate to the reasonable amplitude of 53'.

The weight of the pendulum subjects the spring to a nearly constant stress Mg/ew dyne/cm² (for the meaning of the symbols, see table 5) through the whole of the spring.

There is an alternating stress due to the bending of the spring which reaches its largest (positive or negative) value for each part of the spring at full amplitude. This peak value is largest on the surface of the spring just at the top, viz. $ec/2\rho_0$.

Consider first a spring consisting of one piece of metal forming both spring and ends. Uniformity involves an abrupt change of section at each end, as in *A* of

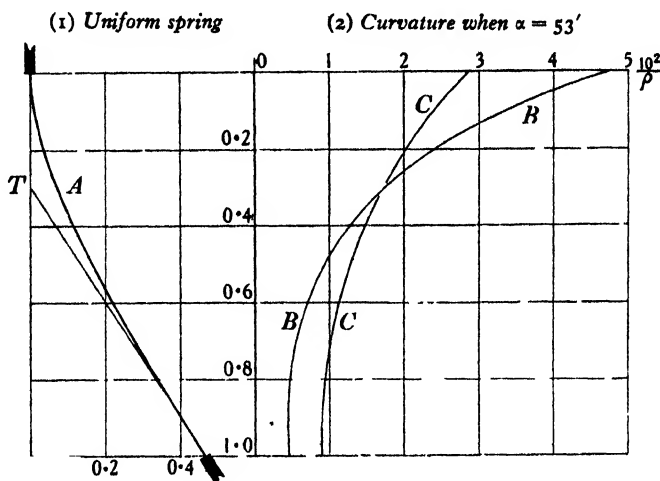


Figure 3. Shape and curvature of uniform suspension spring. *A*, Shape of spring at large amplitude, $\lambda=3.28$; *B*, curvature of this spring, $\alpha=53^\circ$; *C*, curvature of spring 50 per cent thicker than *A* when $\alpha=53^\circ$, $\lambda=1.89$.

Table 5. Uniform springs

Seconds pendulum	e dyne/cm ²	l	Spring	w	c	$\frac{I}{\rho_0}$	Stresses dyne/cm ² $\times 10^8$		λ
							Load- ing	Bend- ing	
$M=7290$ g. $k^2 \dagger = 195$ cm ²	2.13×10^{12}	1.05	1	1.27	0.0148	0.0473	3.80	7.47	3.28
			2	1.27	0.0222	0.0286	2.53	6.78	1.89
			3	4.30	0.0148	0.0286	1.12	4.52	1.89

Spring dimensions: l , length; w , width; c , thickness; all in cm. Young's Modulus, e . The bending stress is the largest one, viz. that on the surface at the top when $\alpha=53^\circ$. Spring properties (shape, effect on rate etc.) are expressed in terms of λ and its hyperbolic functions, where $\lambda=l\sqrt{(12Mg/ec^3w)}$.
 \dagger About centre of mass.

figure 3 and *b* of figure 4. It is well known that abnormal stresses occur in the region of a discontinuity of this kind, but the analysis which provides the figures in table 5 takes no account of these abnormal stresses. Theorists tend to lose sight of them. Thus Keelhoff, in referring to the ground spring, urges that the rounding off between the spring and the thick end should be made very short lest it should invalidate the calculations, "le contraire n'aurait d'ailleurs aucune utilité."*

* *Suspension à Ressort*, p. 16.⁽⁶⁾

The top extremity, then, of this spring is a region of especially heavy stresses at the outside layers. When the spring consists of a thin strip gripped in chaps matters are worse still, because there is movement within the jaws (§ 21) and this cold working will lead to hardening of the metal. The slipping to and fro of the spring surfaces within the chaps accounts for some at least of the losses observed. As the metal hardens there the movement will decrease and so will the loss of energy. Moreover, the spring ceases to be uniform and less of the bending takes place at the top, the turning point of the pendulum (T in figure 3) moves down and the rate increases.

Since a light pendulum supported by a clamped spring has worked satisfactorily, could not a pendulum five times as heavy work well with a similar spring if this is made sufficiently sturdy? In table 5, spring 2 differs from spring 1 only in c which has been increased 50 per cent. This makes No. 2 3.375 times as stiff as No. 1. Figure 3C shows that curvature is much more uniform and the curvature at the top is only 60 per cent of the former value. This, however, is largely offset by the greater thickness, so that the highest bending stress is not materially reduced, and it is increased for most of the spring. It seems, therefore, more hopeful to make the spring wider instead of thicker. To make the same change in λ and in stiffness, the width must be increased to 4.3 cm., making it rather difficult to house the spring. Curvature is the same for No. 3 as for No. 2, and now there is an appreciable fall in the bending stress at the top; but this is spread over 3.375 times the distance. If a clamped spring can avoid secular change with a 7 kg. pendulum, it will, apparently, be a very stiff one and the ground spring, which need not be so stiff, is the more attractive choice.

§ 18. THE NON-UNIFORM GROUND SPRING

In figure 4 four stages are indicated in the development of the suspension spring. The change from the clamped spring (a) to the all-one-piece spring (b) cuts out the working within the chaps. This could probably be effected by soldering the spring in the chaps as Sir Charles Boys has done. There still remains the abrupt change of section which gives rise to abnormal stresses.

When the spring is ground out of the solid (c) the easy transition from uniform spring to rigid end will occur even when the maker does not know that this is an important result.

So long as the rest of the spring is uniform, the top part has the heavy share of bend and stress shown in table 5. The last step, then, is to make the spring non-uniform (d) and leave it somewhat thicker towards the top, so as to make the curvature more uniform.

The theory of the non-uniform spring is difficult compared with that of the uniform spring. J. Haag has stated the general theory fully—the differential equations are there but, except in trivial cases, they have not been solved. In order to obtain information about a suitable section for a spring, it is useless to try to find the shape which a spring of given section will assume as the pendulum swings, because the differential equation stands in the way. If, however, the shape is given,

then the section can be found, for the equation has ceased to be differential. A section can be found, for example, which makes the spring bend into a circular arc. This would not be adopted in practice because the central part of this spring is unnecessarily thick. I have obtained various other solutions, which seem reasonable, based on equalizing the stresses on the surface of the spring rather than the curvature. I do not think that any special form will lead to a perfect spring, but theory can help in deciding how much thickening-up is to be desired towards the top of the spring.



Figure 4. Suspension springs: *a*, uniform spring clamped in chaps; *b*, ends and spring all one piece, abrupt change of section; *c*, ground uniform spring, change of section eased off; *d*, ground non-uniform spring for more uniform curvature.

§ 19. ELINVAR VERSUS STEEL SPRINGS

I was able to use spring *d* for the experiments on component losses because I replaced it on pendulum *E* by a ground elinvar spring. It is not so easy to make a good spring from this as from steel. An alloy called "Isoelastic" is used in America for the coiled springs of weighing machines. Prof. A. W. Price of Toronto has kindly sent me a strip of this material, from which I hope to fashion a suspension

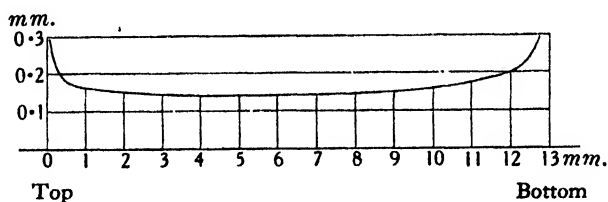


Figure 5. The ground steel spring *d*. Notice easing off into thick ends. The growth in thickness towards the top is desirable. That towards the bottom is detrimental.

spring. Isoelastic may prove more suitable than elinvar for this purpose. At Greenwich the elinvar spring of *SH*, No. 3, has been replaced by a steel one⁽⁹⁾ in order, I suppose, to test whether the secular change of rate can be reduced in this way.

This raises the question whether it is important to secure a zero elasticity coefficient for the spring, when changes can be compensated at the bob and when temperature-control should make even this unnecessary. I think that control is

always imperfect because this relates to air-temperature, which settles bob-temperature, whereas spring-temperature depends partly on the wall (or pillar) temperature where the pendulum is supported. For my clock *F*, which is kept at constant temperature, I have followed the example of the National Physical Laboratory by using auxiliary heating for the brackets, which helps also to maintain a constant temperature-gradient in the sealed case.

Figure 5 shows the contour of spring *d*. The increase of thickness towards the bottom is quite wrong (§ 18). Towards the top end the increase is, I think, insufficient.

§ 20. SPRING *d*. YOUNG'S MODULUS AND PENDULUM RATE

I found by a simple experiment on *d* that a pure couple 8.52×10^4 cm.-dyne bends the spring through 0.128 radian. Suppose that the spring at *x* cm. from one end makes an angle θ with this end under the couple, then the couple is

$$\frac{ec^3w}{12} \frac{d\theta}{dx},$$

whence
$$\theta_1 = \frac{12 \times \text{couple}}{ecw} \int_0^l \frac{dx}{c^3} \quad \dots\dots(6).$$

The measurements used for figure 5 show that the integral $= 3.38 \times 10^5$. It follows that $e = 2.13 \times 10^{12}$, indicating a good quality of steel. A uniform spring of length 1.05 cm., of equal flexibility, and of the same width and material has $1.05/c^3$ equal to 3.38×10^5 , so that $c = 0.0146$ cm. On the other hand, the uniform spring giving the observed frequency with the shortest of the rods suspended from it would be 0.0148 cm. thick and the difference between the two values is a hint that no uniform spring is equivalent to a non-uniform one. The formula giving *n* for a pendulum suspended from a uniform spring is shown in table 6.

Table 6

	<i>S</i> , $\lambda = 3.28$	Rod, 15 cm., $\lambda = 0.309$
$\frac{n^2}{g} = \frac{d + l/\lambda \tanh \lambda}{d^2 + k^2 + dl}$	$\frac{96.72 + 0.32}{9355 + 195 + 101}$	$\frac{8.46 + 11.32}{71.57 + 21.13 + 8.88}$
	$n = \pi$	$n = 13.8$

The centre of mass of the pendulum is *d* cm. below the bottom of the spring. *k* is the radius of gyration about the centre of mass. λ is defined in table 5.

I have given numerical values for the different terms in the formula for the largest and for the smallest of the pendulums used in the experiments. With an ordinary pendulum the second term in the numerator forms a small correction to the main term *d*, but for the short rod it has become the principal term. It is interesting to find how well the formula fits so large a range of cases. For this reason, I have given the computed values of *n* above the observed ones in table 2, but the latter have been used in connection with the experiments.

§ 21. ROD PENDULUMS: SPRING LOSS

In a suspension spring the alternating stress due to bending is combined with the constant stress due to weight and it is not to be expected that a formula which is true in the absence of the latter stress will also apply when it is there. Kimball and Lovell⁽¹⁰⁾ showed that, when an element of volume dV of an elastic body is subjected to an alternating stress whose peak value is S_m , the energy dissipated will be $\xi \times S_m^2 dV$ erg/c. ξ is a constant depending on the material.

Taking the case of a uniform spring and integrating for the whole volume,

$$\text{Loss} = \frac{\xi e l M g \alpha^2}{2} \left(\frac{1}{\lambda \tanh \lambda} + \frac{1}{\sinh^2 \lambda} - \epsilon \right) \text{ erg/c.} \quad \dots\dots(7).$$

Here ϵ represents terms aggregating about 3 per cent of the whole for a seconds pendulum, to which the formula does not apply, but for all the rod pendulums the terms are quite negligible. For all the rods, the constant stress is comparatively small and for these the formula should be nearly true.

Here λ is a proper fraction and the formula can be simplified to

$$\text{Loss} = \frac{\xi e^2 w c^3 \alpha^2}{12 l} \left(1 + \frac{\lambda^4}{45} - 0.004 \lambda^6 \right) \text{ erg/c.} \quad (8).$$

Replacing the non-uniform spring d by the uniform spring of equal flexibility, I find $\lambda = 0.32$ for the shortest rod and 0.75 for the longest. Hence the loss is $\xi \times 3.36 \times 10^{14} \times 1.0002$ for the short rod whilst the last factor is 1.006 for the long one. The greatest loss, then, is only 0.6 per cent larger than that due to a pure couple. Thus the spring loss is practically the same for all the rod pendulums, as has been assumed in § 13.

Assuming that the whole of the observed suspension loss is due to the spring, we have $3.36 \times 10^{14} \xi = 0.182$, or $\xi = 0.55 \times 10^{-15}$. In Kimball and Lovell's list the smallest value of ξ is 0.306×10^{-15} for hard rolled phosphor bronze. Next to this comes 1.10×10^{-15} for swaged nickel ($3\frac{1}{2}$ per cent) steel. Thus, the steel of d comes between these two substances with smallest losses. This seems to confirm the conclusion that for the rod pendulums there is no appreciable bracketing loss.

Kimball and Lovell experimented with flexible rotating bars. They also experimented with springs and make a statement which bears out the conclusions arrived at regarding clamped springs. They say that the vibration tests gave values 2 or 3 times as high as those obtained by the other method: "*considerable energy was dissipated by surface friction in the clamps.*"

§ 22. IMPULSE-LEVER LOSS

The impulse levers for pendulums E and F consist of three arms mutually at right angles, one of which carries the needle points forming the axis, which is placed in line with the axis about which the pendulum turns. The other horizontal arm is weighted and produces a clockwise moment about the axis causing the lower end of

the vertical arm to press towards the left against the pendulum rod or else against the armature lever which moves between two stops. When the pendulum, moving towards the right hand, reaches an angle θ beyond the vertical, it picks up the impulse lever and the two move together to the full amplitude and back again to angle θ on the left hand of the vertical. During this extra (2θ) left-hand movement, the energy necessary for maintenance is supplied to the pendulum.

Observations for decrement may be made (*a*) with the impulse lever entirely out of action, clear of the pendulum, or (*b*) with the armature lever stationary against its right-hand stop and impulse lever in position, the pendulum picks it up as usual at $+\theta$ but, after passing full amplitude, drops it again at $+\theta$, no energy being supplied to the pendulum, or else (*c*) with the armature lever to the left so that the impulse lever moves through the range $-\theta$ to $+\alpha$ and back to $-\theta$.

In (*a*) decrement is due entirely to loss of energy by the free pendulum. In (*b*) there is in addition loss due to the impulse lever, this being less than the loss when the lever is impulsing, and in (*c*) the additional loss is greater than this latter loss by an equal amount.

In order to find the lever loss, then, the decrement for (*a*) is subtracted from the mean of the decrements for (*b*) and (*c*). The lever loss is, however, so small compared with the pendulum loss that it cannot be observed with an ordinary pendulum which the lever is intended to impulse. The losses with rod pendulums being smaller, I made one of these which beat nearly half seconds and obtained the results shown in columns 7 and 8 of table 2, showing a loss due to the lever of 0.045 erg/c.

Apart from frictional losses there is loss of energy due to the inelastic collision when the pendulum meets the lever. This collision imparts energy to the lever, which is lost when the lever is arrested at $-\theta$, and there is further loss of energy as heat. When mk^2 for the lever is very small compared with MK^2 for the pendulum, the equation resulting from the principle of conservatum of angular momentum shows that these two amounts of energy are virtually equal and that their sum $= mk^2\dot{\theta}^2 = mk^2n^2\alpha^2\cos^2\tau$, $\theta/\alpha = \sin\tau$. With $\theta = 25'$ and $\alpha = 53'$, the loss due to collision is 0.037 erg/c.

Turning again to the experimental result, comparing the larger amplitudes with the smaller ones I find that the loss for the former is too small compared with that for the latter. To get an accurate value for so small a quantity, it would have been necessary to repeat the experiment many times. I feel justified, however, in concluding that the total loss is not greatly in excess of that due to the collision and, for want of more exact information I think it best to adopt this calculated value for the impulse lever loss. Hence the value 0.04 erg/c. for H given in table 3.

For $S(n = \pi$ as compared with 2π for H) the collision loss is reduced to 0.01 erg/c., which is the figure I have inserted in table 3. I suppose that the total lever loss is at most less than 0.02, which is about one-thousandth part of the pendulum loss.

Prof. Sampson says of Cottingham's lever that its loss "appears to amount to one-tenth of what is required for free maintenance." I have not seen this clock, but in making my lever I was following Sampson's description of Cottingham's. I cannot suppose that any lever could dispose of 2 erg/c.

My lever weighed 2.93 g. The horizontal arm from axis to centre of gravity is small. In order to increase this arm and thus the constancy of impulse, I have reduced the weight of the lever to 0.7 g., of which nearly one-third is at the solid end of the horizontal arm. This lighter lever has, however, a moment of inertia larger than that of the old lever. For these new levers, I sought in vain for tubes with thin walls and had to make these myself out of 0.001-in. german-silver foil with silver-soldered seams.

§ 23. EFFECT OF ENCLOSING PENDULUM IN CASE

H is normally enclosed in an inverted propagating glass with the bob about half way up. This case adds about 16 per cent to the total loss and so about 30 per cent to the resistance experienced by the bob. When the air pressure is reduced by 200 mm. the loss is about the same as at full pressure in the open. *S* is housed in a glass cylinder 122 cm. long and 20 cm. in diameter. This adds somewhat less than 20 per cent to the decrement and again reduction to about 550 mm. restores the open-air amplitude.

I have no experience with pendulums working in gas at low pressures.

I have not found the opportunity for repeating the experiments on loss components with greater precision. In the hope that another investigator will do so, I have taken care to point out the short-comings of these experiments.

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DISCUSSION

For discussion see p. 753.

THE AMPLITUDE DEVIATION OF RATE OF A PENDULUM: A SECOND EXPERIMENT

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ABSTRACT. In a previous experiment the amplitude deviation was almost equal to the circular deviation. The present experiment was made on a lighter pendulum with a long suspension spring, moving in different surroundings. The amplitudes ranged from 108' to 224' as compared with the previous range of 30' to 70'. The deviation is about 15 per cent larger than the circular deviation and is well represented by the latter plus a linear term. Two other experiments with Graham's escapement are referred to, in which the driving weights are varied. One of these, described by Sir Henry Cunynghame, seems to be hypothetical, for it yields an amplitude giving a minimum rate instead of a maximum one. Guillaume overlooked the large temperature effect produced by an invar suspension spring, which the author found by experience and calculated. Prof. R. A. Sampson sought to find the deviation by observations on a Shortt clock without allowing for impulse deviation. It is pointed out that the deviation for the master pendulum when it is impulsed is less than the deviation for the pendulum when it is free. In addition to the vibration used for time-keeping, a spring-suspended pendulum has a parasitic mode of vibration which the concentrated Shortt impulse is well adapted to set up. Prof. Sampson has analysed the author's previous experiment by the method of least squares and concludes that the solution given is but one of a number of possible solutions. Neither of Sampson's alternatives is a least-squares solution and both involve impossible values of the decrement. The corrected normal equations confirm the original solution.

§ 1. NEED FOR A SECOND EXPERIMENT

TWO years ago I described experiments⁽⁹⁾ with a spring-suspended pendulum vibrating in air, which showed amplitude deviation agreeing closely with the circular deviation calculated for motion about a centre in vacuo. The result for this pendulum, E_{11} , does not necessarily hold good for other pendulums. For this reason, I tested a grandfather clock by changing the driving weight from time to time during ten weeks in the winter 1936-7.

Until fifteen years ago, this clock was just a good household clock made almost 140 years ago. Then I provided it with a new pendulum which was bracketed to the wall through the back of the clock case. This change converted it into a first-class time-keeper, but not into a precision one. Minor changes followed, and in 1936 I made a new pair of Graham pallets, taking care to make the front faces truly dead, so that the impulse deviation could be correctly calculated.

This seconds pendulum, G , is contrasted with E_{11} of the previous experiment, in table 1. G has a light bob and a very long suspension spring. The long, narrow

Table 1. Two experiments compared

The pendulums

	Bobs			Rods		Case (cm.)	Air pressure (mm.)	Suspension spring				
	Height (cm.)	Dia- meter (cm.)	Weight (g.)	Dia- meter (cm.)	Weight (g.)			Length <i>l</i>	Width <i>w</i>	Thick- ness <i>c</i>	Young's modulus <i>e</i>	λ
E_{11} (1934)	16.0	7.4	5740	0.8	440	cylinder diam. = 20	540	1.08	1.27	0.014	1.7×10^8	3.96
G (1936-7)	9.6 1.6	4.1 2.4	1430 60	0.32	70	46×10 (at bob 7.5)	750	2.54	0.66	0.021	1.5×10^8	3.63

G has an auxiliary bob for regulating and a plate opposite to the bob to prevent air reaction between the driving weight and the bob. $\lambda = l\sqrt{(12Mg/ec^2w)}$. M is the total mass of the pendulum.

Range of observations

	Amplitude	Rate (sec./day)
E_{11}	30' to 70'	0.4 to 2.2
G	108' to 224'	6.2 to 26.2

space in which it moves probably involves more air drag than does the cylindrical case of E_{11} . The space is further reduced opposite to the bob by a shield, which prevents air reaction between the bob and the driving weight.

The range of amplitudes, too, is different in the two experiments. Hence there is a range of rates in the second experiment ten times as large as in the first, which makes up for the larger errors in rate and amplitude which must be expected.

In this paper definitions and explanations given in the previous one will not in general be repeated. Even for the largest amplitude α involved, the circular deviation is represented with sufficient accuracy by $86400 \times \alpha^2/16$ sec./day, when α is expressed in radians.

§ 2. RESULTS FOR PENDULUM G

The results for pendulum G are shown in table 2. The alphabetical sequence is that of amplitude, the numerical sequence, column 2, shows the order of events, large and small amplitudes being taken roughly alternately in order to reduce the

Table 2. Amplitudes and rates [+ means losing rate]

1 Period	2 Order	3 Days	4 Driving weight (kg.)	5 Ampli- tude (mins.)	6 p.e. angle (mins.)	7 Equiv. p.e. (sec./day)	8 Rate (sec./day)	9 p.e. (sec./day)	10 Impulse devia- tion	11 Free pendu- lum	12 Circular devia- tion
<i>a</i>	2	8	1.10	108.6	0.8	0.08	0.49	0.05	1.61	-1.12	5.39
<i>b</i>	7	10	1.55	124.8	0.7	0.08	2.05	0.07	1.31	+0.74	7.11
<i>c</i>	4	8	2.07	147.0	0.5	0.06	5.28	0.04	1.06	4.22	9.88
<i>d</i>	5	10	2.72	164.8	0.8	0.12	8.03	0.13	0.96	7.07	12.41
<i>e</i>	3	6	3.68	188.6	0.3	0.05	12.58	0.10	0.88	11.70	16.25
<i>f</i>	1	10	4.42	203.7	0.7	0.13	15.19	0.18	0.83	14.36	18.96
<i>g</i>	6	8	5.85	223.8	0.6	0.12	19.68	0.09	0.75	18.93	22.89

effect of a possible drift in rate. With reference to the driving weights, the clock was originally worked by 5.2 kg., but the usual weight now is 1.5, the reduction being partly due to reduced amplitude and largely due to the reduction in loss of energy effected by fixing to the wall. Amplitude is measured on a fixed scale, over which the pointed end of the rod moves. The probable error of amplitude observations is given in decimals of a minute of arc and converted, by the result of the experiment, into seconds per day (col. 6), for comparison with the probable error for rate (col. 9). The two are roughly of the same order, namely 0.1 sec./day.

The rates given in column 8 are the observed rates, reduced to 29.5 in. by applying a barometric correction of 0.4 sec./day per inch. This is the observed variation when $\alpha = 126'$ and includes the remote effect due to the change of amplitude. For the larger angles it is, therefore, likely to be too large. No correction has been applied for temperature (§ 7), and no barometric correction has been applied to amplitudes.

Rates were obtained by daily comparisons with the 10.0-h. Greenwich rhythmic signal, amplitude and barometer being observed about the same time.

Free pendulum rates, column 11, are found by deducting impulse deviation, column 10, from observed rates.

§ 3. FITTING A FORMULA TO THE OBSERVATIONS

Geometrical considerations suggested two solutions which were then computed by the method of least squares. If the free pendulum rates (ordinates) are charted

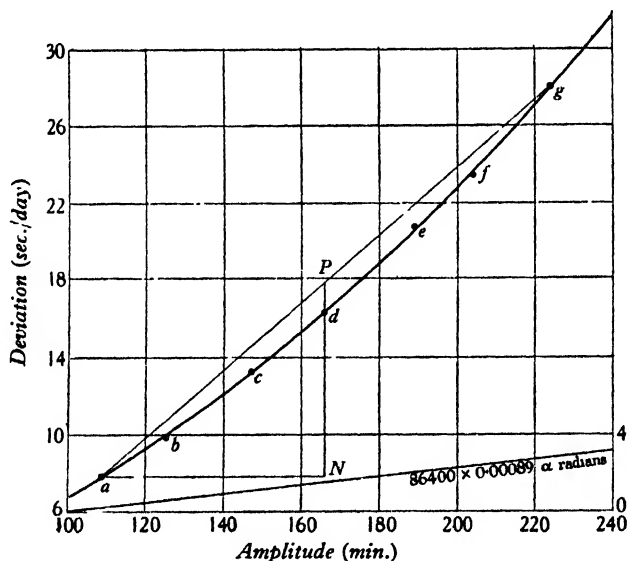


Figure 1. Amplitude deviation. Solution B. Circular deviation $+0.0244m$, where amplitude is in minutes of arc. The curve is a computed one, whilst the points are observed amplitude deviations.

against amplitudes (abscissae), we are at liberty to move the whole group vertically so that the lowest point *a* lies on any curve, for we are concerned only with relative rates, absolute rate being merely a question of regulation; see figure 1.

For another point, say g , to be on the curve at the same time, the range for the two points (20.05 sec./day) must be the same as the range for the curve. The corresponding circular deviation range is only 17.50 sec./day, and this must be increased by about 15 per cent to include the two points. The middle point d will lie on a curve containing a and g if the vertical distance Pd of d from ag is equal to the corresponding intercept between the chord and arc of the curve. Now, for the points

$$\begin{aligned} Pd &= PN - dN \\ &= \frac{164.8 - 108.6}{223.8 - 108.6} \times 20.05 - (7.07 + 1.12) \\ &= 1.59 \text{ sec./day.} \end{aligned}$$

For circular deviation, the corresponding calculation gives 1.51 sec./day. This intercept is 5 per cent less than for the points. There are two simple ways of modifying circular deviation to embrace a and g : (A) We may use a multiple—about 1.15—of it, and (B) we may add a linear term $x\alpha$ to it. (A) will increase the intercept to about 1.73, which is too large for d ; (B) will leave it at 1.51, which is too small for d . This suggests a combination of (A) and (B). These considerations concern only three out of seven points and have taken no account of errors due to observation and to erratic behaviour of the clock.

§ 4. TWO FORMULAE

Solution (A) is expressed by the formula

$$x \times \text{circular deviation} = \text{free pendulum rate} + y,$$

whilst for (B) we have

$$\text{circular deviation} + x \times \text{amplitude} = \text{free pendulum rate} + y.$$

For finding x and y in each case, there are seven equations of condition which have been reduced to the necessary two equations for finding x and y by the method of least squares. I find

$$(A) \text{ free pendulum rate} + 7.23 = 1.147 \times \text{circular deviation} \quad \dots\dots(1),$$

$$(B) \text{ free pendulum rate} + 8.99 = \text{circular deviation} + 77\alpha \quad \dots\dots(2).$$

Rates are given in table 2, columns 11 and 12. Circular deviation = $86400 \times \alpha^2/16$, α here and in the linear term of equation (2) being measured in radians. Thus in equation (2) $\alpha^2/16$ becomes $\alpha^2/16 + 0.00089\alpha$. When α is expressed as m' (minutes of arc), 77α becomes $0.0224m$.

Figure 1 shows solution (B), the sloping straight line showing the linear contribution starting from an arbitrary zero at 100'. Table 3 compares the observed with the computed rates for the two formulae. In (A) the central part of the curve is too low (column 4) whilst the extreme parts are too high: the curvature is too great, which agrees with § 3. In (B) examination of the residuals does not suggest whether the curvature is too large or too small—the erratic variations are too large. The graph gives the impression that no appreciable improvement on solution (B) is

Table 3. Two curves representing rates

A				B		
1 Amplitude (mins.)	2 Free pen- dulum +7.23 (sec./day)	3 $1.147 \alpha^2$ 16	4 Observed minus calculated	5 Free pen- dulum +8.99	6 $\frac{\alpha^2}{16}$ +0.00089 α	7 Observed minus calculated
108.6	6.11	6.18	-0.07	7.87	7.82	+0.05
124.8	7.97	8.15	-0.18	9.73	9.90	-0.17
147.0	11.45	11.35	+0.10	13.21	13.17	+0.04
164.8	14.30	14.24	+0.06	16.06	16.10	-0.04
188.6	18.93	18.64	+0.29	20.69	20.47	+0.22
203.7	21.59	21.74	-0.15	23.35	23.51	-0.16
223.8	26.16	26.25	-0.09	27.92	27.89	+0.03
Root mean square				0.154		
				0.117		

In columns 3 and 6 the formulae have been multiplied by 86,400 to give values in seconds per day.

possible: the main offenders e and f will be respectively above and below any smooth curve. The root mean squares of the residuals show that (B) is a distinctly better solution than (A). I offer (B) as a suitable formula for pendulum G. It can be put in the form free pendulum rate + 9.26 = 86400 ($\alpha + 0.007$)²/16, but this does not suggest to me any theoretical meaning for the linear term.

§ 5. THE IMPULSE DEVIATION

If a uniform impulse is delivered to the pendulum commencing when it is θ_1' past the vertical and lasting to θ_2' , this will cause the pendulum to lose

$$86400 \frac{\delta}{n} \tan \frac{\tau_1 + \tau_2}{2} \text{ seconds per day}^{(12)}, \quad \dots\dots(3)$$

where δ is the decrement, $n = 2\pi \times \text{frequency} = \pi$ for a seconds pendulum, and $\sin \tau_1 = \theta_1/\alpha$, $\sin \tau_2 = \theta_2/\alpha$. I measured θ_1 and θ_2 by fixing a millimetre scale just above the fork of the lever so that it moved with the pallets. The index consisted of several lines not uniformly spaced. In this way I eliminated, I hope, personal errors in estimating fractions of the millimetre. The beat is adjusted so that θ_2 is the same when escape is from the right pallet as from the left. Then the two θ_1 values are not so nearly equal as I had hoped. For calculating deviation I used the average value. Pivot friction adds largely to the decrement of the pendulum. To secure uniform action it is important for the fork to touch the pendulum on one side only. Hitherto I have secured this by means of a counterpoise, which serves the purpose, but produces a reaction in the bearings and adds to the friction. When amplitude was to be doubled for this experiment, the counterpoise was increased, and with it the decrement. I have now replaced the counterpoise by a light spring at the fork pressing on the other side of the pendulum rod.

Table 2 shows that the change in impulse deviation is less than 5 per cent of the change in rate, so that errors in determining the former do not have an appreciable effect on the result.

§ 6. IMPULSE DEVIATION BALANCING AMPLITUDE DEVIATION

The slowing effect of a dead-beat impulse falls off (see table 2, column 10) with increasing amplitude, whilst the amplitude deviation increases. Equation (3) shows that the deviation, and also its rate of decrease with increase of α , is increased by increasing $\frac{\tau_1 + \tau_2}{2}$, i.e. by retarding the impulse and especially by delaying the release of the scape wheel.

Theory indicates that with a much retarded impulse and for amplitudes of, say, 120', impulse deviation falls more rapidly than amplitude deviation grows, i.e. rate increases with amplitude. Eventually, of course, the latter deviation takes the upper hand, so there is a maximum rate for some angle if the amplitude is changed by increasing the driving weight. Prof. David Robertson has shown me a chart, which Mr A. E. Ball of Messrs Gent sent to him in 1925, relating to a Graham regulator, showing a maximum rate of this kind.

Sir Henry Cunynghame⁽¹⁾ describes the experiment of changing the driving weights with a Graham escapement. He states that a minimum rate will be found and that this is somehow due to friction on the dead faces. I conclude that he had not tried the experiment himself. With reference to this escapement he quotes Airy's formula, but says that the impulse increases the rate.

§ 7. TEMPERATURE ERROR DUE TO SUSPENSION SPRING

When I first installed this pendulum, I was at a loss to explain the very large increase of rate with temperature. As the clock was operating in the open air, the decrease of air-density with rise of temperature would cause an increase in rate which might easily balance, and more than balance, the slowing due to growth of the invar rod and bobs, but this did not suffice to explain why the main bob must be supported a considerable distance above its top. Later the explanation became clear. I had used invar for the spring as well as for the rod and I had omitted to take account of the growth of its elasticity with temperature. I erred in good company, for Dr Guillaume⁽²⁾, the inventor of invar and of elinvar, deals with the compensation of a pendulum, supplied with an invar spring, in great detail yet omits all reference to the spring except to remark that had it been made of steel allowance would have to be made for the variation in its length.

When λ is as large as with this pendulum (table 1), $\tanh \lambda \div 1$ and the formula for rate becomes

$$\frac{n^2}{g} = \frac{d + l/\lambda}{d^2 + k^2 + dl} \quad \dots\dots(4),$$

where d is the distance (cm.) between the bottom of the spring and the centre of mass of the pendulum; hence for a rise of 1° C.

$$\frac{dn}{n} = \frac{l}{4\lambda d} \frac{de}{dT} \quad \dots\dots(5),$$

where T is the temperature (° C.),

$$\frac{de}{dT} = +5.0 \times 10^{-4} \text{ for invar, } -2.4 \times 10^{-4} \text{ for steel, } \pm 0.5 \times 10^{-4} \text{ for Elinvar.}$$

Here are figures about the compensation of *G*, with its main bob of lead 9.6 cm. high and with a brass tube above this screwed to the rod 7.5 cm. up, for a rise of 1° C. The increases are in sec./day.

Expansions, invar and bobs	-0.015	Top half of lead bob	-0.052
Air	+0.037	7.5 cm. of brass tube	-0.054
Spring	+0.075		
	+0.097		-0.106

I do not know any of the coefficients accurately. Since this final compensation in 1928, I do not know whether the pendulum is under-compensated or not. Consequently, in the deviation experiment, I have made no corrections for temperature.

§ 8. DATA FROM A SHORTT PENDULUM

Prof. R. A. Sampson⁽³⁾ sought to find amplitude deviation from a series of observations of pressure amplitude and rate of SH_4 at Edinburgh in 1930 when the case was leaking. Assuming that the rate could be expressed by the formula

$$x + y \times \text{pressure} + z \times \text{circular deviation},$$

x being a constant, y the increase of rate per inch pressure and z a fraction, sixteen equations of condition were reduced to three by the usual method of least squares. On eliminating x Sampson found that the two equations for y and z were nearly identical and so concluded that the formal solution would have no value. He remarked that from an inspection of the chart he concluded that z was about $\frac{3}{4}$, i.e. that the clock would not show full circular deviation. Since no allowance was made for impulse deviation, the deviation that Sampson refers to is that of the impulsed master pendulum, which is less than that of the same pendulum when free.

As this Shortt master pendulum is often referred to as a "free pendulum", I will discuss the difference.

§ 9. THE SHORTT IMPULSE

Part (a) of figure 2 shows the method of applying the impulse, which consists in allowing the jewelled end of a lever to roll down a small wheel attached to the pendulum. The first part of the thrust is very small when the contact is near the top of the wheel, but it increases rapidly with ϕ , and, but for the inertia of the lever, would increase indefinitely until the contact point was in line with the centre of the wheel and the lever axis. In that case, the diagram of the impulse would be the curve T in figure 2, viz. $k \tan \phi$ (ordinate) plotted against $\sin \phi$ (abscissa). The actual diagram is indistinguishable from T in the early stages. I_1 indicates (purely diagrammatically) the later stages of the impulse, which is seen to depart more and more from T as angular acceleration of the lever increases, until a maximum is reached, followed by a rapid fall to zero, before the three points come into line.

With amplitude reduced owing to rising density of air, during Sampson's observations, the accelerations become less for all positions, so that the new diagram I_2 keeps nearer to T , rises to a higher and later peak, and ceases later than before. This change is appreciable only in the later stages of the impulse shown in figure 2 which usually take place after the pendulum is past the vertical. The black part of the diagram indicates the increased impulse, which with normal timing slows the rate of the pendulum and so wipes out part of the free pendulum deviation. Moreover, the phase of all the post-vertical part of the impulse is retarded by reduction of α and this adds further to the slowing of the rate.

If, then, the free pendulum deviation is just equal to the circular deviation, the resultant deviation of the impulsed master pendulum will be a proper fraction of the circular deviation.

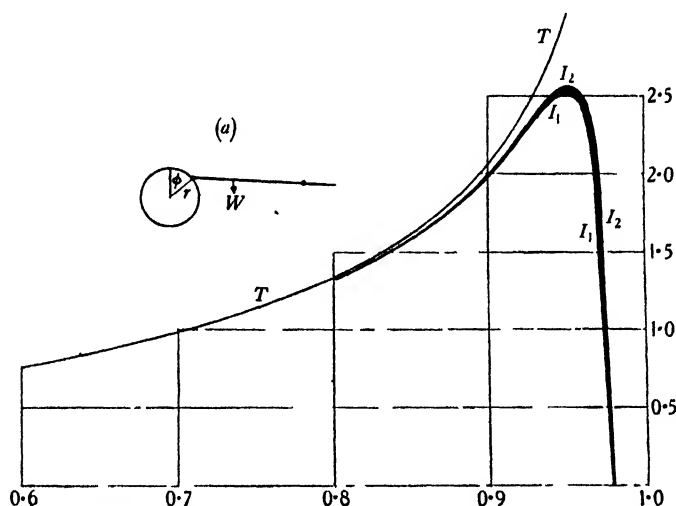


Figure 2 Shortt impulse Change with amplitude

The impulse could, of course, be so timed that for one value of the amplitude the change of impulse deviation is zero.

§ 10. THE PARASITIC VIBRATION

A spring-suspended pendulum has two modes of vibration and its motion is generally compounded of these two modes. It can turn about a point, usually a little above the centre of the spring: this mode is used for time-keeping. The other mode which J. Haag⁽⁴⁾ calls the "parasitic vibration" is made apparent when the top of the rod of a stationary pendulum receives a blow. In this case the turning point is below the centre of mass of the pendulum. If the impulse could be delivered at this point, it would expend all its energy on the wanted vibration. When the impulse is delivered near the top of the rod, some of the energy takes the form of the parasitic vibration, the more so as the impulse approximates to a blow. The Shortt impulse, with sharp peak, is of a type for producing the second mode, especially as the whole of the energy lost in half a minute is replaced by a single impulse, after the previous parasitic vibration has died out.

I do not think that the presence of the second mode of vibration is harmful for time-keeping, but it adds to the difficulties of computing the effect of the Shortt impulse⁽¹³⁾.

§ 11. PROF. SAMPSON'S ANALYSIS OF E_{11} RESULTS

In the same paper, Prof. Sampson analysed the results of my E_{11} experiment⁽¹⁰⁾ by assuming that the observed clock rate

$$a = x + by + cz,$$

where x is a constant, y is the fraction of impulse deviation b which is 'sensible', z is the similar fraction of the circular deviation (see § 13), on the basis of the figures given in tables 1 and 2 of the 1936 paper.

There are eight equations of condition which lead by the method of least squares to three normal equations. These normal equations give values of x , y and z which yield a minimum value of Σv^2 , the sum of the squares of the residuals in the equations of condition, a residual v being the difference between an observed value a and a computed value $x + by + cz$. I quote from Sampson's paper: "Eliminating x [from the normal equations] we have

$$\text{from (1) and (2)} \quad y - 0.494z = +0.511,$$

$$\text{from (1) and (3)} \quad y - 0.508z = +0.504$$

which are almost the same.

"Treated in this way, the observations are quite unequal to separating the two desiderata. Indeed, what choice we may take makes little difference to the constant arrived at. Thus, take $y = 1.00$ then $z = 1.00$, $x = -1.10$, which is Atkinson's solution; but if we take $y = 0.90$ then $z = 0.80$, $x = -1.07$, which is the value indicated on p. 60; but if we take $y = 0.76$ then $z = 0.50$, $x = -1.06$, which is the value Bloxam reached. I conclude, therefore, that Atkinson's data are insufficient to settle the question but that his agreement is evidence that he has chosen one out of a number of possible solutions."

This would, of course, be true if the equations to which Sampson refers were equations of condition with coefficients affected by experimental error, for small changes in such coefficients make large changes in the values of the unknowns and values of these, which only nearly satisfy the equations, such as those given above, might be regarded as solutions. But the equations are normal equations, derived from equations of condition, for finding values for x , y and z that yield a minimum value of Σv^2 . The equations are exact, so that there is, of course, but one solution. If Σv^2 for this solution is not a minimum the equations are wrong. The fact that the two equations for y and z are nearly equal makes solution more laborious, but it introduces no uncertainty as to the result.* The three equations as printed yield a

* Dr R. d'E. Atkinson points out that this fact reduces the weight of the value found for z . In this sense, uncertainty is introduced, as is shown by the large value of the probable error.

negative value for z . It appears that 11.51 in equation (2) should be 11.61. With this correction, the two equations for y and z follow approximately correctly and yield $z=0.5$ —Bloxam's value. A more exact solution of Sampson's equations is $x=1.039$, $y=0.772$, $z=0.528$. Calculating the residuals and expressing them in msec./day I find $\Sigma v^2=12,545$, as compared with 916 for the correct solution and 1232 for $z=1$. The solution, then, is not a least-squares solution and the normal equations are wrong.

I have recomputed these equations and, profiting by Sampson's experience that two significant figures vanish in the last stage of solution, I have sought to secure accuracy in the fourth decimal place in each coefficient by computing each product to five places. It should be remembered that the equations are exact and that a value determined to three places only, such as 19.592, means 19.5920 for the purposes of solution.

§ 12. THE CORRECT NORMAL EQUATIONS

The normal equations are:

$$8x + 19.592y - 8.436z = 2.372 \quad \dots(1),$$

$$19.592x + 59.3568y - 26.2817z = 11.6250 \quad \dots(2),$$

$$8.436x + 26.2817y - 11.7269z = 5.3228 \quad \dots(3),$$

from (1) and (2) $y - 0.494197z = 0.511253,$

from (1) and (3) $y - 0.503599z = 0.501881,$

whence $0.009402z = 0.009372,$

$$z = 0.997 \pm 0.039,$$

$$y = 1.004 \pm 0.019,$$

$$x = 1.111 \pm 0.007 \text{ sec./day.}$$

With these values the residuals are $-2, +20, +4, -17, -13, +6, -1, -1$ msec./day, while $\Sigma v^2=916$ as compared with 12,545 for the wrong solution. This result is a neat confirmation of the conclusions arrived at in the 1936 paper, where the solution is $y=z=1$. With regard to the value 0.997 for z , I pointed out that "amplitude deviation appears to grow slightly less rapidly than circular deviation. No importance can, however, be attached to the differences. . . changes in δ of less than 0.5 per cent would wipe out all the differences." I chose a value for x which gave smaller percentage values for the residuals than the least-squares solution.

Where the two penultimate equations are nearly equal the computation of a least-squares solution is unusually arduous. This method is not the only one for reducing the number of equations of condition to the number of equations needed for a unique solution^(5, 6, 7, 8). Other methods applied to the present case agree in showing that values of y and of z are in the neighbourhood of unity.

§ 13. THE IMPULSE DEVIATION

In the preceding two sections, I have dealt with an analytical problem without reference to the physical meaning of the quantities concerned.* Prof. Sampson's research depended on the possibility of *systematic* error in the determination of impulse deviation amounting to as much as 25 per cent. I referred to two possible sources of error and I did not, perhaps, indicate clearly enough the possible effects. I pointed out that whereas steady amplitudes were ascertained to 0.01', the angle at which the pendulum picked up the impulse lever was known less accurately. If an error of

Table 4. Three curves for E_{11}

Losing rates (sec./day)				
Period	Observed rate	Residuals (observed - calculated)		
		$z = 1.0$ $y = 1.0$ $x = 1.102$	0.8 0.905 1.08	0.5 0.761 1.035
<i>a</i> 5	0.723	+ 3	+ 27	+ 73
<i>b</i> * 1, 6, 7, 8	-0.054	- 6	+ 17	- 36
<i>c</i> 2	-0.600	0	- 15	- 47
<i>d</i> 3	-1.022	- 12	- 9	- 24
<i>e</i> 4	-1.331	- 17	+ 11	+ 35
Root mean square		0.010†	0.017	0.046
Intercept (§ 3) Percentage	0.226	+0.007 3	-0.034 15	-0.100 44

* Weighted mean for 4 periods each with $\alpha = 39.7$.

Prof. Sampson treats these as separate results, but this makes little difference.

† With $x = 1.102$ the residuals have smaller *proportional* values than with $x = 1.095$, for which the root-mean-square value is 0.007.

0.1' was committed in finding this, the range of 3.9 sec./day in the deviation would be 0.008 sec./day in error: less than $\frac{1}{4}$ of one per cent. Then I referred to the determination of decrement as being "the weakest link in the experimental chain". Figure 3, p. 614 shows a series of points, each representing an experimental determination and a line drawn among the points which was used for reading off values of δ/n needed for computing the deviation. There is no systematic error in the points⁽¹⁴⁾; such an error can only come from wrong judgment in drawing the line. A line drawn 1 per cent lower down is clearly wrong (the zero line is not at the bottom of the figure but is near to the bottom line of print of the page), and a line 2 per cent down clears all the points, save two manifestly erratic ones. I think individual values of the deviation may possibly be 1 per cent in error, but a systematic error of this order is highly improbable.

For small changes of amplitude it is permissible to express amplitude *error* (i.e. rate of change with amplitude of amplitude *deviation*) as $z \times$ circular error:

* Apart from the method of solution, table 4 shows that 0.8 and 0.5 of the circular deviation (last two columns) give unsatisfactory fits for the observed rates as compared with full circular deviation, the curves being too flat for the points.

z may change with α . To assume for a range of amplitude (from 30' to 70') that amplitude deviation = $z \times$ circular deviation is not safe.

The deviation of pendulum G is not satisfactorily expressed in this way. With knife-edge suspension, the law of deviation may be entirely different from this⁽¹¹⁾.

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DISCUSSION

Dr A. L. RAWLINGS. There are two or three matters in the paper on dissipation about which I should like to ask Mr Atkinson for more information. In his oral comments this evening he said he had not the means either to attain or to measure very low air pressures in his clock case. From the kinetic theory of gases it is sometimes argued that no substantial reduction of air resistance is to be anticipated unless the pressure is reduced to vanishing point. Some of Mr Atkinson's results—for instance those mentioned after equation (4)—seem contrary to this theory. Does Mr Atkinson think that the elimination of the last $\frac{1}{4}$ in. or so of air pressure would lead to an important diminution of air resistance?

It may be of interest to mention some results obtained with the spinning wheels of gyro compasses as having some bearing on this question. The Sperry compass used in our navy has a steel wheel a foot in diameter and 2 in. thick spun at about 8600 r.p.m. by a built-in electric motor. The wheel is closely surrounded by a casing which is exhausted to about 1 in. of mercury by a very simple hand pump to reduce the power taken by the motor. My own experiments show that when the casing is so exhausted the total power fed into the electrical system is 240 watts. If air at atmospheric pressure is admitted to the casing, the speed of the wheel drops to 6800 and the watts put in rise to 420. Since there is a large fixed loss in the motor, this seems to show that the residuum of windage loss at the lower pressure is very small. Again, if the current is cut off when the wheel is spinning at 9000 r.p.m., its speed falls to half value at the low pressure in 70 minutes, or at atmospheric pressure in 12 minutes.

In considering the impulse-lever loss it has to be remembered that whereas the end of the lever describes an arc of a circle, the pendulum rod which it touches describes some other curve, so that at the point of contact there is rubbing friction which may assume a large value. Every one knows how the absence of a little oil at the crutch of a common clock may make it refuse to go at all. The losses described in § 22 as due to the impulse lever are therefore astonishingly small, and lead one to wonder whether the form of the ground suspension spring has the further advantage of constraining the pendulum to move more nearly in a circular arc.

Dr O. KANTOROWICZ. In recent years the investigation of what is called the damping capacity of engineering materials has become of some importance. As a rule these experiments are made by clamping a rod-shaped test piece into a machine in which it undergoes free torsional oscillations, whose decay is observed and taken as a measure of the damping capacity. In order to avoid additional damping by slip between the rod and the clamps holding it, the clamps are pressed against the rod with great force. It has been considered sufficient to exert on the clamps such a force that the stress per unit of the macrogeometrically described contact area approaches the yield point. Do the author's experiments give any indication whether this assumption is justified?

In order to obtain a uniform bending of suspension springs the author proposes to grind these springs so that they shall be thicker at the suspended end than at the free end. A similar result can of course be obtained by using a spring of uniform thickness and gradually increasing the width of the strip towards the fixed end. I suppose a spring of this form would have smaller internal losses than the spring proposed, on account of the maximum stresses being smaller, since the damping capacity grows with a rather high power of the surface stress.

Mr HOPE JONES. If Mr Atkinson could tell us how much energy was dissipated in the flexure of the suspension spring, and how much was expended in moving the pendulum's apparently rigid support, he would do us good service. I have never experienced difficulty in measuring the total energy dissipated by a pendulum swinging in air or vacuum. One knows the foot-pounds required to maintain it at a certain arc by means of a *Synchronome remontoire*: remove the maintenance and note the time taken in the fall of the arc, as a check upon the weight of the lever, multiplied by the distance of its fall. That simple procedure was impossible in the bad old days of escapements, when such elemental truths could not be disentangled from the escapement errors which masked them.

May I express the hope that the author will describe his escapement and his method of resetting the gravity lever? Does he use the *Synchronome remontoire*? On page 739 he describes the well-known modification of the Grimthorpe gravity escapement, in which the pendulum is relieved of the duty of unlocking, but he does not say how the gravity lever is replaced. The pendulum collides with a gravity arm, carries it up to the end of its swing, and returns with it to a lower point, the difference between its lift and fall being the impulse. Variation of arc involves

variation in the value of that impulse. The distance which the pendulum* has to carry a gravity arm uphill cannot be varied with impunity, particularly since it happens in that part of the path where it should be a point of honour to leave the pendulum alone. Mr Cottingham speaks of it as Gill's, but it was really due to Froment. The names of Liais and Verité in France were associated with it, and later on, Tiede and Knoblich in Germany, whilst LeRoy of Paris calls it Reid-Winnerl, but they are all fundamentally the same. Gill's greatest trouble was contact and his greatest mistake was to provide an impulse every second instead of at long periods. R. J. Rudd made a real free pendulum two years before Gill produced his semidetached escapement based on Froment's. Had they met then, the world would probably not have had to wait another twenty years for a free pendulum.

Mr E. T. COTTINGHAM. With a given suspension it would seem that it needed minute change in form for each particular bob, since the bending point rises with increase in weight of the bob. With thin suspension springs, which some prefer, I feel that critical molecular changes may occasionally occur, from causes little suspected, such as rapid oscillatory changes in their potential caused by a flash of lightning in the vicinity of the clock, or even the slower change in potential due to a passing cloud.

The Foucault effect, due to the earth's rotation, although constant, may be more unfavourable to the clock in certain latitudes. At the poles it exerts a torsional effect on the pendulum; at other places it would act obliquely across the suspension, at the angle of the latitude where the clock is fixed; but at the equator it would act across the bending point of the spring, its most favourable point, and here it may be involved in the true beat of the clock and the zero position of the pendulum. As our present practice makes lighter pendulums possible, I think the knife-edge suspension offers some advantage over the spring. I, too, was concerned in 1912 with probable movement of the support of a pendulum in a heavy iron case resting on three points, until the thought of Newton's rings prompted me to hold two +0.5 D. spectacle lenses in contact with the support by a rod fixed to the wall, with the happy result that the blue ring showed only a slight change in tint with alternate swings of the pendulum, an amount that mirrors or micrometers would not show. I agree with Mr Hope Jones that two other people had used the escapement before the late Sir David Gill, who lent me his drawings, but he was not aware of it, and their illustrations of it were rather crude. Sir David was the first to use it under precision conditions, and that is why I prefer to associate his name with it. Mr Hope Jones's comparison of the Gill clock with the Grimthorpe gravity escapement is not a good one, as the former, like the renowned Shortt, is freed from the frictions of unlocking and has an almost frictionless gravity arm resting on needle points in agate cups, in perfect alignment with the bending point of the spring. The lifting of this by the pendulum, some time before it reaches the end of its swing, disturbs it no more than the rapidly increasing impulse of some escape-

Dr R. D'E. ATKINSON. The energy-losses due to a clamped suspension spring are similar to those we found when investigating the damping of torsional oscillations in quartz fibres. No form of clamp that we tried was adequate; not even that obtained by fusing the fibre, after drawing it, into a lump of pyrex. When we drew the fibre from a rod and retained both ends of the rod on the fibre we got decrements about 100 times smaller than had previously been obtained by any means. The resulting shape was of course analogous to that produced in a suspension spring by grinding.

The question what degree of vacuum is adequate to make the damping due to residual gases negligible naturally depends on the magnitude of the other damping agents, but I think the figure of 0.001 mm. given by the author is not too low.

I should like to ask the author if he has looked into the question whether a spring could be so ground that the path of the bob would be cycloidal, so as to eliminate the circular error?

For the AUTHOR'S REPLY see page 856.

AN X-RAY INVESTIGATION OF ATOMIC VIBRATIONS IN MAGNESIUM BETWEEN 86° AND 293° K.

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ABSTRACT. Measurements are made of the intensities of X-ray reflections from magnesium powder at 86° and 293° K. Absolute values of the ratio I_{002}/I_{100} are obtained by making comparative measurements on a composite specimen of magnesium and aluminium powders. The results are discussed in relation to theoretical work by Zener and others on the effect of lattice vibrations in hexagonal metals on the intensities of X-ray reflections. It is shown that in magnesium the lattice vibrations are almost isotropic but that the mean atomic displacements in the basal plane are about 3 per cent greater than those parallel to the c axis. Values are calculated for the mean atomic displacements in these directions at 86° and 293° K., and the results are also expressed in terms of characteristic temperatures Θ_0 (parallel to the c axis), equal to 339°, and Θ_{90} , equal to 327°. A consideration of these results, in conjunction with similar results for other hexagonal metals, points to a correlation between the departure of the axial ratio from the ideal value 1.633 and the asymmetry of the lattice vibrations.

§ 1. INTRODUCTION

THE results of X-ray investigations of the asymmetry of the lattice vibrations in hexagonal metals carried out during the last few years by one of us^(1,2) in this laboratory and by Jauncey, Wollan and others^(3,4,5,6) in St Louis, U.S.A., when considered collectively, point to a correlation between the asymmetry of the vibrations and the departure of the axial ratio from the ideal value, 1.633, calculated for a hexagonal close-packed system of spherical atoms having isotropic vibrations. For zinc^(1,3,6) and cadmium⁽²⁾, which have axial ratios 1.856 and 1.886, the amplitude of the atomic vibrations is markedly greater in the direction of the c axis than in the basal plane, whereas for Ag-Cd⁽⁴⁾ and Cu-Zn alloys⁽⁵⁾ in the ϵ phase, each having an axial ratio of 1.56, the amplitude of vibration is greater in the basal plane than in the direction of the c axis. In order to test more thoroughly the idea that the axial ratio gives an indication of the nature of the lattice vibrations, we thought it desirable to examine a metal with an axial ratio approximating to the ideal value, 1.633, and have therefore investigated the case of magnesium, which has an axial ratio of 1.624. The experiments have shown that the lattice vibrations are very nearly isotropic but have a slightly (about 3 per cent) greater amplitude in the basal plane than normal to it, and hence provide additional support for the view that there is a correlation between the departures of the axial ratios from the ideal value, 1.633, and the asymmetry of the lattice vibrations.

§ 2. EXPERIMENTAL

The experimental procedure has been to measure the intensities of X-ray reflections from finely powdered magnesium at room-temperature and at the temperature of liquid air. The change in the magnitude of the atomic vibrations between these temperatures is sufficient to cause a measurable change in the reflected intensities, and from the ratio of the intensities at the two temperatures from different lattice planes the amplitudes of the atomic displacements can be calculated as a function of the temperature and of direction in the crystal lattice.

The method adopted for measuring the intensities resembles that previously described⁽⁷⁾ in that the incident radiation is reflected by a flat layer of powder at the centre of a cylindrical camera, and the reflections are recorded on a concentric cylindrical film surrounding the camera. For measurements at liquid-air temperatures we have modified the powder-holder so that it has the form of a shallow cavity 0.5 mm. deep, 2 cm. long and 0.5 cm. wide, in a flat copper sheet at the end of a thin-walled brass tube containing the liquid air; the lower end of this container was of semicylindrical form constructed so that the front surface of the copper sheet was on the axis of the camera, and, since the copper was only 1 mm. thick, the powder was separated from the liquid air by only about 0.5 mm. of metal. To minimize the heat radiation falling on the powder, when the latter has been cooled to liquid-air temperature, from other parts of the camera at room-temperature, the powder-holder was surrounded as completely as possible with copper shields cooled to liquid-air temperature; the X rays pass to and from the powder through a narrow gap in these shields. Throughout these experiments the camera was kept evacuated and became, in effect, a Dewar vessel; this was essential at the lower temperature and was useful also at room-temperature, since it facilitated the maintenance of the temperature at a constant value, namely, 20° C. We have taken the temperature of the powder when it is cooled with liquid air to be 86° K., with an uncertainty of not more than 2°, which is less than 1 per cent of the full temperature range. This value was checked by thermocouple measurements and also by measuring the change in the position of high-order reflections from silver powder when cooled from the temperature of the room to that of liquid air. The entire technique has been checked by measurements on aluminium powder, which showed close agreement with previous measurements by James, Brindley and Wood⁽⁸⁾ on single crystals of aluminium cooled from the temperature of the room to that of liquid air, and also with results calculated from the Debye-Waller theory. While this work was in progress a paper by Wollan and Harvey⁽³⁾ has appeared which describes briefly a camera of somewhat similar construction.

With this type of camera, no difficulties are encountered in measuring the relative intensities of reflections at low temperatures other than those encountered at room-temperature. Absolute values of the reflected intensities were obtained by comparing reflections from magnesium and aluminium powders intimately mixed in a suitable mass-ratio. Wollan and Harvey⁽³⁾ have recently advocated the use of magnesium oxide as a useful comparison substance since the change of intensity

with temperature is very small and can be calculated from the characteristic temperature by means of the Debye-Waller theory. Magnesium oxide is not very suitable as a comparison substance for magnesium, owing to the positions at which the reflections occur; we have preferred aluminium since the reflections are conveniently situated and also because the experiments of James, Brindley and Wood⁽⁸⁾ on single crystals of aluminium, and our own (unpublished) measurements on aluminium powder, show that between the temperature of the room and that of liquid air, the intensities of reflection obey closely the Debye-Waller theory.

Measurements were made with copper $\kappa\alpha$ radiation on two separate specimens of magnesium powder prepared by light filing with a Grobet no. 5 file. Previous (unpublished) work by one of us (G. W. B.) on magnesium has shown that it is extremely difficult to prepare specimens of magnesium powder of the flat-layer type which do not show a preferential orientation of the basal plane towards the surface of the layer, and this effect is very marked in the specimens used in the present experiments owing to the strong pressure that must be exerted on the specimens in order to obtain compact powders having good thermal conductivity. We have not, therefore, utilized our intensity-measurements to obtain the scattering factor f for magnesium. Since we are here interested only in the change of the intensities with temperature, preferential orientation of the crystallites is of no importance provided the measurements at both temperatures are made with the powder surface at the same angle to the incident X-ray beam, and special care was taken to satisfy this condition.

§ 3. RESULTS

The experimental results are set out in table 1; part (a) of the table gives the intensities of the reflections relative to 100.0 for the $1\bar{1}2\bar{2}$ * reflection for the two specimens of powder at the two temperatures, together with the probable percentage errors calculated from the expression

$$\text{probable error} = 0.6745 [(\Sigma \delta^2)/n(n-1)]^{\frac{1}{2}},$$

where n is the number of observations and $\Sigma \delta^2$ is the sum of the squares of the residuals. To obtain sufficiently accurate results a large number of films has been measured, and for each film always two and sometimes three independent measurements have been made across different parts of each reflection. In calculating the probable error we have taken for n the number of films measured rather than the total number of measurements; hence the accuracy may be somewhat better than is indicated by the probable percentage errors given in the table.

Part (b) of the table summarizes the results for the ratio of the intensities at 86° and 293° relative to unity for the $1\bar{1}2\bar{2}$ reflection; the second and third columns give this ratio for the two specimens separately, and the fourth column gives the mean

* The reflecting planes in a hexagonal lattice are usually indexed with respect to four axes. The first three, the a axes, are taken in the basal plane of the structure at intervals of 120° , while the fourth, the c axis, is the hexagonal axis of the lattice and is thus perpendicular to the a axes. It can be shown for any plane that if the indices corresponding to two of the a axes are h, k , then the index corresponding to the third is $\bar{h} + \bar{k}$. Thus the indices of a plane are expressed in the form $(h, k, \bar{h} + \bar{k}, l)$.

ratio. In calculating the probable errors, we have taken for the separate ratios the sum of the errors in the quantities involved, and for the mean ratio, which depends on approximately twice as many observations as the separate ratios, we have taken the mean of the errors in the separate ratios divided by $\sqrt{2}$.

Table 1. Intensities of X-ray reflections at 86° and 293° K.

(a) Relative intensities

Reflections	Specimen I				Specimen II			
	I_{293}	Probable error (per cent)	I_{86}	Probable error (per cent)	I_{293}	Probable error (per cent)	I_{86}	Probable error (per cent)
11 $\bar{2}2$	100.0	—	100.0	—	100.0	—	100.0	—
20 $\bar{2}1$	63.2	0.7	61.9	0.5	62.8	0.6	62.5	0.6
0004	38.0	0.8	38.6	0.8	36.7	0.8	37.4	0.8
20 $\bar{2}2$	24.3	1.1	25.3	1.3	21.6	1.0	23.6	1.1
10 $\bar{1}4$	39.4	1.1	42.9	1.3	39.4	1.0	41.6	1.2
20 $\bar{2}3$	63.1	0.9	70.5	1.1	60.4	1.0	68.7	0.8
21 $\bar{3}1$	84.3	1.2	98.7	1.1	80.2	1.1	96.5	0.8
11 $\bar{2}4$	98.0	1.3	115.0	0.9	96.0	1.0	111.6	0.9
10 $\bar{1}5$, 21 $\bar{3}2$	113.3	1.2	136.7	1.1	111.0	0.9	134.8	1.0
21 $\bar{3}3$	77.8	1.9	104.8	1.0	74.5	1.3	100.5	1.1

(b) Relative and absolute values of I_{86}/I_{293}

Reflections	I_{86}/I_{293} , relative to 1.000 for Mg 11 $\bar{2}2$						I_{86}/I_{293} absolute
	Specimen I	Probable error (per cent)	Specimen II	Probable error (per cent)	Mean	Probable error (per cent)	
11 $\bar{2}2$	1.000	—	1.000	—	1.000	—	1.237
20 $\bar{2}1$	0.980	1.2	0.995	1.2	0.988	0.8	1.222
0004	1.016	1.6	1.019	1.6	1.018	1.1	1.260
20 $\bar{2}2$	1.041	2.4	1.098	2.1	1.067	1.6	1.320
10 $\bar{1}4$	1.089	2.4	1.056	2.2	1.073	1.6	1.326
20 $\bar{2}3$	1.118	2.0	1.138	1.8	1.128	1.4	1.396
21 $\bar{3}1$	1.171	2.3	1.204	1.9	1.188	1.5	1.470
11 $\bar{2}4$	1.174	2.2	1.163	1.9	1.168	1.4	1.445
10 $\bar{1}5$, 21 $\bar{3}2$	1.208	2.3	1.215	1.9	1.210	1.5	1.497
21 $\bar{3}3$	1.347	2.9	1.349	2.4	1.348	1.8	1.667

(c) Data for standardizing the relative values of I_{86}/I_{293}

Reflections	I_{86}/I_{293}		Absolute values relative values
	Relative values, table 1b	Absolute values, table 2	
11 $\bar{2}2$	1.000	1.255	1.255
20 $\bar{2}1$	0.988	1.205	1.220
20 $\bar{2}3$	1.128	1.394	1.238
			Mean 1.237

From the data given in parts (a) and (b) of the table it is seen that although the relative intensities of reflection from the two specimens at the two temperatures

show differences of the order of several per cent, the ratios of the intensities are in much closer agreement. The differences in the relative intensities may have arisen partly from differences in the degree of orientation of the crystallites, and partly from a small difference in the angular settings of the powders with respect to the incident beam, since the angles were measured only to the nearest 0.5 degree. It is satisfactory to find that the agreement between the ratios of the intensities comes well within the limits of probable error for all the reflections except the 20 $\bar{2}$ 2 which was by far the weakest reflection measured. The probable errors in the measured intensities are of the order of 1 per cent, and this is the highest accuracy to be expected from the photographic method of measuring intensities. It is obtainable only by careful measurement of a large number of films, and the labour involved is considerable; altogether in this part of the investigation 46 films have been measured, and two or three independent determinations have been made for each reflection on each film. Comparing the measurements at 86° and 293° we see that the probable errors are slightly less at 86°, and this fact is most marked for the higher order reflections.

Table 2. Comparison of intensities reflected by magnesium and aluminium at 86° and 293° K.

Reflections	Relative intensities		Probable error (per cent)		(I_{86}/I_{293})	
	293° K.	86° K.	293° K.	86° K.	relative	absolute
Al 220	100.0	100.0	—	—	1.000	1.118 ₆
Mg 10 $\bar{1}$ 3	121.8	129.2	0.5 ₆	0.6 ₁	1.06 ₁	1.18 ₇
Mg 11 $\bar{2}$ 2	104.9	117.6	0.7 ₄	0.5 ₈	1.12 ₁	1.25 ₅
Mg 20 $\bar{2}$ 1	66.9	72.0	1.2 ₁	1.0 ₈	1.07 ₇	1.20 ₆
Mg 20 $\bar{2}$ 3	54.5	67.9	1.3 ₉	1.2 ₃	1.24 ₆	1.39 ₄

In order to obtain absolute values of the ratio I_{86}/I_{293} , the intensities of the 10 $\bar{1}$ 3, 11 $\bar{2}$ 2, 20 $\bar{2}$ 1 and 20 $\bar{2}$ 3 reflections from magnesium were compared with the 220 reflection from aluminium at the two temperatures; 13 films in all were measured at 293° K. and 15 films at 86° K. The results are set out in table 2, where the columns, in order, give the indices of the reflections, the reflected intensities at 293° and 86° relative to 100.0 for aluminium 220, and the probable percentage errors calculated as before. The sixth column of the table gives the ratio of the intensities at the two temperatures relative to unity for aluminium 220, and the seventh column gives the absolute value of this ratio calculated in the following manner. From their work on single crystals of aluminium, James, Brindley and Wood⁽⁸⁾ showed that the exponent M in the equation

$$I_T = Ie^{-2M} \quad \dots\dots(1),$$

which gives the intensity I_T reflected at a temperature T in terms of the intensity I reflected by the atoms at rest, has the form

$$M = (h^2 + k^2 + l^2) \{3.87 \times 10^{-5} T + 0.177/T - 277/T^3\} \quad \dots\dots(2),$$

where h , k and l are the indices of the reflections. This expression gives for I_{86}/I_{293} for aluminium 220 the value 1.118₆ and it is in terms of this result that we have

standardized our values of the ratio I_{88}/I_{293} for the magnesium reflections. Comparing now the relative values of I_{88}/I_{293} in column 6 of table 1b for the magnesium reflections 11 $\bar{2}$ 2, 20 $\bar{2}$ 1 and 20 $\bar{2}$ 3 with the corresponding absolute values in column 7 of table 2, we see from table 1(c) that the mean conversion factor from relative to absolute values of I_{88}/I_{293} is 1.237 and hence we obtain the absolute values of I_{88}/I_{293} given in the final column of table 1(b).

§ 4. DISCUSSION

The main question at issue is to determine whether the lattice vibrations in magnesium between 86° and 293° K. are isotropic, and, if not, to discover the magnitude of the anisotropy. It has been shown⁽⁹⁾ that the exponent M in the equation for the effect of temperature on the reflected intensity, equation (1), is given by

$$M_\psi = 8\pi^2 \overline{u_\psi^2} (\sin \theta/\lambda)^2 \quad \dots\dots(3),$$

where $\overline{u_\psi^2}$ is the mean square displacement in a direction ψ normal to the reflecting planes. In the case of hexagonal crystals, it may easily be shown, as Zener⁽¹⁰⁾ first pointed out, that the mean square displacement in a direction ψ with respect to the c axis can be expressed in terms of the mean square displacements parallel and perpendicular to the c axis, by the equation

$$\overline{u_\psi^2} = \overline{u_0^2} \cos^2 \psi + \overline{u_{90}^2} \sin^2 \psi \quad \dots\dots(4).$$

Alternatively, we may write

$$M_\psi = M_0 \cos^2 \psi + M_{90} \sin^2 \psi \quad \dots\dots(5).$$

For cubic crystals it has been shown by Debye and Waller that

$$M = \frac{6h^2 T}{mk\Theta^2} [\Phi(x) + x/4] (\sin \theta/\lambda)^2 \quad \dots\dots(6),$$

where Θ is the characteristic temperature which occurs in the Debye theory of specific heat, $x = \Theta/T$, and $\Phi(x)$ is the well-known Debye function. The expression in square brackets, the so-called quantization factor, may conveniently be represented by Q and is of the order of unity provided $T > \Theta$ or $T \sim \Theta$. It follows from the work of Zener, Jauncey and their collaborators^(10, 11), that a formula similar to equation (6) may be applied to crystals of lower symmetry provided Θ is regarded as a function of the direction in the crystal and, at high temperatures, also of the temperature. For hexagonal crystals we may write

$$M_\psi = \frac{6h^2 T}{mk} \left(\frac{Q}{\Theta^2} \right)_\psi (\sin \theta/\lambda)^2 \quad \dots\dots(7),$$

or, from equation (5),

$$M_\psi = \frac{6h^2 T}{mk} \left[\left(\frac{Q}{\Theta^2} \right)_0 \cos^2 \psi + \left(\frac{Q}{\Theta^2} \right)_{90} \sin^2 \psi \right] (\sin \theta/\lambda)^2 \quad \dots\dots(8).$$

This equation can be compared with the experimental results as follows:

We have

$$\log_e (I_{88}/I_{293}) = 2 (M_{293} - M_{88}) = 2\Delta M,$$

whence

$$\begin{aligned}\frac{\log_e (I_{86}/I_{293})}{(\sin \theta/\lambda)^2} &= \frac{12h^2}{mk} \left[\Delta \left(\frac{TQ}{\Theta^2} \right)_0 \cos^2 \psi + \Delta \left(\frac{TQ}{\Theta^2} \right)_{90} \sin^2 \psi \right] \\ &= \frac{12h^2}{mk} \left[\left\{ \Delta \left(\frac{TQ}{\Theta^2} \right)_0 - \Delta \left(\frac{TQ}{\Theta^2} \right)_{90} \right\} \cos^2 \psi + \Delta \left(\frac{TQ}{\Theta^2} \right)_{90} \right] \dots\dots(9),\end{aligned}$$

where the symbol $\Delta (TQ/\Theta^2)$ denotes the change in (TQ/Θ^2) between 86° and 293° K. This last equation indicates that if the atomic vibrations in magnesium are anisotropic, there should be a linear relation between the experimentally determined quantity $\log_e (I_{86}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$ and $\cos^2 \psi$ from which Θ_0 and Θ_{90} may be calculated. If, however, the vibrations are isotropic, the coefficient of $\cos^2 \psi$ in equation (9) will be zero and $\log_e (I_{86}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$ will have a constant value from which a mean Θ for the crystal can be obtained.

In table 3 the observed reflections are recorded in order of the angle ψ , which is calculated from the relation

$$\cos \psi = (l/R) \{4(h^2 + kh + k^2)/3 + (l/R)^2\}^{-1/2} \dots\dots(10),$$

where h , k and l are the indices of the reflection. The columns of the table, in order, give the indices of the reflections, $(\sin \theta/\lambda)$, ψ and $\cos^2 \psi$; the final column gives $\log_e (I_{86}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$ together with the probable errors calculated from those in the seventh column of table 1(b). The percentage errors in the quantity

$$\log_e (I_{86}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$$

are of the order of 4 per cent for the majority of the reflections, and this is to be compared with corresponding errors of the order of 1.5 per cent in the ratios (I_{86}/I_{293}) . This increase in the probable error arises in taking the natural logarithm of the measured ratio.

Table 3. Values of $\log_e (I_{86}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$

Reflections	$\left(\frac{\sin \theta}{\lambda}\right)$	ψ	$\cos^2 \psi$	$\log_e (I_{86}/I_{293}) \cdot (\sin \theta/\lambda)^2$	
0004	0.384	0°	1.000	1.56 ± 0.08	
1014	0.425	25.1	0.820	1.57 0.09	
1013	0.340	32.0	0.719	1.48 0.07	
1124	0.495	39.1	0.602	1.50 0.06	
1015	0.513	20.5	0.877	} 0.582	1.53 0.05
2132	0.514	68.0	0.140		
2023	0.462	51.3	0.391	1.56 0.06	
1122	0.367	58.4	0.275	1.58 —	
2133	0.557	58.8	0.268	1.64 0.06	
2022	0.408	61.9	0.222	1.66 0.10	
2021	0.373	75.1	0.066	1.44 0.06	
2131	0.487	78.6	0.039	1.62 0.06	

The results show that if there is a variation of $\log_e (I_{86}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$ with $\cos^2 \psi$ it can only be small; hence any departure from isotropic vibrations must be very small. It is difficult to decide whether there is any real variation in this quantity or whether the departures from a constant value are to be interpreted

simply as experimental errors. The arithmetical mean value is 1.56, and most of the values agree with this mean value within the limits of the probable errors. We have, however, examined the results by the method of least squares in order to find the best linear equation to fit them. Writing equation (9) in the form

$$\frac{\log_e (I_{98}/I_{293})}{(\sin \theta/\lambda)^2} = m \cos^2 \psi + c,$$

we find the following values for m and c :

$$m = \frac{12h^2}{mk} \left\{ \Delta \left(\frac{TQ}{\Theta^2} \right)_0 - \Delta \left(\frac{TQ}{\Theta^2} \right)_{90} \right\} = -0.114$$

$$c = \frac{12h^2}{mk} \Delta \left(\frac{TQ}{\Theta^2} \right)_{90} = 1.632$$

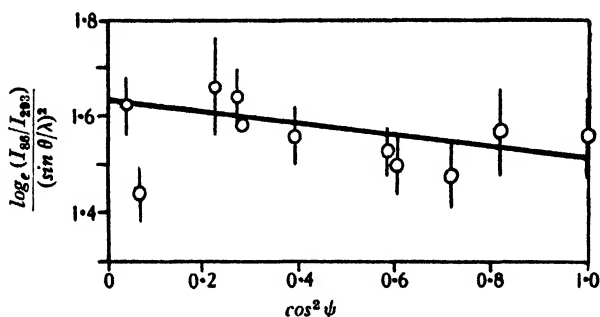


Figure 1. Observed values of $\log_e (I_{98}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$ plotted against $\cos^2 \psi$. The straight line is calculated by the method of least squares.

The straight line given by these values of m and c is shown in figure 1 together with the experimental values of $\log_e (I_{98}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$; the vertical line attached to each point indicates the probable error. We see that the straight line passes through the points within the limits of experimental error, with the single exception of the 2021 which lies so far from the most probable straight line that it was neglected in calculating the best values of m and c . For the two reflections 1015 and 2132, which are not resolved, we have calculated a weighted mean value of $\cos^2 \psi$ by weighting the separate values of $\cos^2 \psi$ with the relative intensity of the reflection assuming the scattering factor f for each reflection to be the same; this procedure admittedly gives results which are only approximate, but it serves to show that the measurement in question is not in disagreement with the general run of the others. In view of the uncertainty as to the best way of obtaining a mean $\cos^2 \psi$ for this reflection, we have not included it in the calculation of the constants for the mean line.

With the values given above for m and c , we obtain

$$\Delta \left(\frac{TQ}{\Theta^2} \right)_{90} = 1.744 \times 10^{-3}$$

and

$$\Delta \left(\frac{TQ}{\Theta^2} \right)_0 = 1.620 \times 10^{-3},$$

whence, by a graphical solution,* we obtain

$$\left. \begin{aligned} \Theta_0 &= 339^\circ \\ \Theta_{90} &= 327^\circ \end{aligned} \right\}.$$

Assuming that the probable errors in m and c are of the same order as in the quantity $\log_e (I_{98}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$, namely 4 per cent, we find that the corresponding errors in Θ_0 and Θ_{90} are $\pm 7^\circ$. The difference between Θ_0 and Θ_{90} is therefore of the same order as the sum of the probable errors, a result which agrees with the previous statement that the individual values of $\log_e (I_{98}/I_{293}) \cdot (\sin \theta/\lambda)^{-2}$ agree with the mean value within the limits of error. We consider, however, that the tendency of the values shown in figure 1 to decrease with increasing $\cos^2 \psi$ is a real effect and that, although the measurements cannot be made with sufficient accuracy to give a reliable value of the difference of Θ_0 and Θ_{90} , they are sufficiently accurate to establish the result that Θ_0/Θ_{90} is slightly greater than unity and hence, as we shall proceed to show, that the mean atomic displacement in the direction $\psi=0$, the c axis, is slightly less than the mean displacement in the direction $\psi=90^\circ$, the basal plane, approximately in the ratio 327/339. Combining equations (3) and (7), we have

$$\begin{aligned} \overline{u_0^2} &= \frac{3h^2 T}{4\pi^2 mk} \left(\frac{Q}{\Theta_0^2} \right), \\ \overline{u_{90}^2} &= \frac{3h^2 T}{4\pi^2 mk} \left(\frac{Q}{\Theta_{90}^2} \right). \end{aligned}$$

Taking for Θ_0 and Θ_{90} the values 339° and 327° , we obtain the following:

$$\begin{aligned} \text{at } T &= 293^\circ \text{ K.,} & (\overline{u_0^2})^{\frac{1}{2}} &= 0.125 \text{ \AA.} & \text{and} & (\overline{u_{90}^2})^{\frac{1}{2}} &= 0.130 \text{ \AA.,} \\ \text{at } T &= 86^\circ \text{ K.,} & (\overline{u_0^2})^{\frac{1}{2}} &= 0.078 \text{ \AA.} & \text{and} & (\overline{u_{90}^2})^{\frac{1}{2}} &= 0.080 \text{ \AA.} \end{aligned}$$

$$\text{Also } \Theta_{90}/\Theta_0 = 0.96_6$$

$$(\overline{u_0^2})^{\frac{1}{2}}/(\overline{u_{90}^2})^{\frac{1}{2}} = 0.96_6 \text{ at } 293^\circ \text{ K. and } 0.97_1 \text{ at } 86^\circ \text{ K.}$$

An average value of $\overline{u^2}$ for all directions has been calculated from the relation

$$\overline{u_{av}^2} = \frac{\overline{u_0^2} + 2\overline{u_{90}^2}}{3},$$

whence an average characteristic temperature, Θ_{av} , has been derived. We find $(\overline{u_{av}^2})^{\frac{1}{2}}$ has the values 0.128 \AA. at 293° K. and 0.080 \AA. at 86° K.; the corresponding values of Θ_{av} are 331° at both temperatures. This value of Θ_{av} is of the same order as the value 290° obtained from specific-heat data⁽¹³⁾, but the difference is appreciable and may perhaps be explained along the lines suggested in a recent paper by Blackman⁽¹²⁾.

§ 5. CONCLUSIONS

The lattice vibrations in magnesium between 86° and 293° are shown to be almost isotropic, the root-mean-square displacements being about 3 per cent greater in the basal plane than parallel to the c axis; this small difference can only be

* We have plotted $\Delta(TQ/\Theta^2)$ against Θ for a range of values of Θ , from $\Theta=300^\circ$ to $\Theta=380^\circ$; over this range the relation is almost linear.

established very approximately, but the measurements are sufficiently accurate to justify the conclusion that there is a small asymmetry in the lattice vibrations, the amplitude being slightly greater in the basal plane, and of the order of magnitude stated. When this result is considered in relation to the results of previous measurements on hexagonal metals, § 1, the total evidence points strongly to the conclusion that there is a correlation between the departures of the axial ratio from the ideal value 1.633 and the asymmetry of the lattice vibrations; metals with c/a greater than 1.633 appear to have mean atomic displacements which are larger parallel to than normal to the c axis, and vice versa. Magnesium, with c/a equal to 1.624, approximates to the ideal but shows a small asymmetry in the lattice vibrations consistent with the axial ratio being slightly less than 1.633.

§ 6. ACKNOWLEDGEMENTS

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CRITICAL FREQUENCY MEASUREMENTS OF WIRELESS WAVES REFLECTED OBLIQUELY FROM THE IONOSPHERE

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ABSTRACT. Experiments are described which compare the *F*-region skip frequency, for transmission between two distant stations, with that calculated from the normal-incidence characteristics on a simple ray theory. The greatest possible accuracy was aimed at so that the results might resolve an uncertainty left in previous measurements, in which the forms of the oblique and normal incidence *P'f* curves were compared. This involved using a pulse-transmitter at each end of the oblique trajectory to correct for horizontal variations of ionization, and developing a special rapid technique. Measurements were confined to days when the ionosphere was in a completely undisturbed state, as shown by the clean splitting of echoes at normal incidence.

The results showed that the theory, which neglects the earth's magnetic field, is very nearly correct for the ordinary wave over a transmission distance of about 500 km. The precise disagreement is determined, and it is believed that if an accurate theory be developed the results will indicate whether or not the Lorentz term should be included in the analysis.

§ 1. INTRODUCTION

MEASUREMENTS of the ionization-density in the ionosphere are now available in many parts of the globe. Apart from their physical interest these measurements are made with the object of predicting the transmission characteristics for a trajectory joining any two points. Their use in this way, however, depends entirely on a knowledge of the relationship between vertical and oblique propagation conditions for a given ionized region, and little information is as yet available about this relationship. It is with the object of deriving experimental evidence on this point that the present work has been carried out.

A simple theory relating the group times of travel of two waves, incident vertically and at a known angle on the ionosphere, has been given by Martyn⁽¹⁾. This theory neglects the earth's magnetic field and also the possible effect of the Lorentz term⁽²⁾, but it serves as a useful guide as to the behaviour to be expected at oblique incidence. In a previous paper⁽³⁾ it was shown how, from a normal-incidence *P'f* curve, the corresponding curve (relating equivalent path and frequency) for transmission between two distant points could be deduced by means of this theory, and some experimental results were given which showed good qualitative agreement with the theory. The measurements were made, however, with a transmitter at one end only of the oblique trajectory, and it was not known to what extent the departures

found from the simple theory were due to variations of ionization along the path of the wave.

The present paper is an account of a series of experiments in which normal-incidence measurements were made at each end of the trajectory, so that the ionization conditions prevailing at the mid point could be found by interpolation. The technique was developed so as to permit the maximum accuracy in the comparison of normal-incidence and oblique-incidence phenomena. The present discussion of the results is limited to a comparison with the simple theory previously given: it is believed that if later a more complete theory taking into account the earth's magnetic field can be developed, the results will also provide evidence as to whether or not the Lorentz polarization term should be included in the theory.

§ 2. SPECIAL CONSIDERATIONS

Accurate experiments of the type proposed can only be carried out when the ionosphere is in an entirely undisturbed state. The previous experiments had shown that region *E* was generally far too irregularly stratified for useful measurements to be made, and it was decided therefore to confine attention to region *F*. This region also is often in an unsuitable state, the disturbance having the effect of broadening the echoes just before their penetration, and measurements were therefore made only on those occasions when the echoes at normal incidence showed clean splitting even when retarded up to an equivalent height of 800 km. In these cases it was found that the results showed good consistency among themselves.

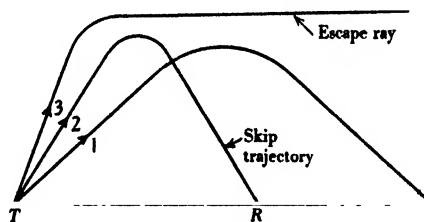


Figure 1

The previous work had shown that the form of the {equivalent-height, frequency} curve for the distant transmission agreed well with that derived by use of the simple theory. In the present work, therefore, most of the experiments consisted in measuring accurately, and as nearly simultaneously as possible, the final skip frequency in the oblique transmission, and the normal incidence $P'f$ curve, so that the exact relationship between them could be found. It is to be noted that the limiting frequency for oblique transmission is fundamentally different from that of penetration at normal incidence: it represents a trajectory which does not reach to the height of maximum density in the layer but is formed by the convergence of the two trajectories present before the skip is reached; see figure 1. It therefore does not involve an increase of absorption as the limiting frequency is approached. On the contrary, the signal strength tends to increase with frequency owing to the focusing effect of the layer on this limiting wave, and the result is, in practice, to

make the final frequency extremely well defined. The final frequency is therefore particularly suitable as a quantity for accurate measurement in experiments of this type.

The method of calculation used previously is tedious when a large number of curves are to be handled, and when only the limiting frequency was required it was calculated from the normal-incidence $P'f$ curve by means of a more rapid graphical method due to Smith⁽⁴⁾. This depends on the same theory as the previous method. It may be stated briefly as follows.

A wave of frequency f incident at an angle i on the ionosphere has an equivalent path given by Martyn's theorem

$$P'(f, i) = \sec i \cdot P'(f \cos i, 0),$$

where $P'(f \cos i, 0)$ is the equivalent path at normal incidence and frequency $f \cos i$.

Breit and Tuve⁽⁵⁾ have shown that, if d is the distance of transmission, then

$$P'(f, i) = d \operatorname{cosec} i.$$

Hence, on elimination of $P'(f, i)$,

$$P'(f \cos i, 0) = d \cot i.$$

Curves are plotted for the fixed distance d and for selected values of f (the oblique-incidence frequency) relating P' to the normal incidence frequency $f \cos i$. The angle of incidence is a variable parameter along any one of these curves. Any curve then shows the equivalent height that must exist at normal incidence and frequency $f \cos i$ if the higher frequency f is to be propagated at an angle i to the distant receiver. The curves are placed over the experimental $P'f$ curve for normal incidence, and it is evident that the highest frequency which can be reflected to the distant receiver is given by the particular curve which is tangential to the observed $P'f$ relationship; see figure 2. The family of curves derived by the above method depends only on the ground distance between the transmitter and receiver, and once plotted it can therefore be applied to all the experimental results. The calculation by this method also shows, by the point of tangency, the equivalent height on the normal-incidence $P'f$ curve which corresponds to the top of the oblique-incidence trajectory. This is of interest in showing what part of the ionosphere is ultimately responsible in reflecting waves to a given distance.

The distance of transmission used in the experiments was 464 km. For this condition the curvature of the earth is just appreciable, and its effect has been allowed for to a first approximation by adding to the equivalent heights measured at the end stations a distance which represents the departure of the earth's surface at the mid point from the chord joining the transmitter and receiver (figure 3). This distance is 4.5 km. in the present instance.

The two magneto-ionic components are propagated independently at oblique incidence, as at normal incidence, and it was shown in the previous work that the {equivalent-path, frequency} curves for each were of the form that would be expected from the normal-incidence curves. Most of the present measurements were made

on the ordinary wave alone, since this was likely to be the less affected by the field, and also because the measurements on it were more reliable since the extraordinary wave was always present after the penetration, showing that the signal had not been lost through any other cause. Since at normal incidence the ordinary wave is reflected from a height independent of the field, it is probable that the effect of the field on this wave at oblique incidence will be small, in which case we may expect the calculation based on Martyn's theorem to agree closely with experiment.

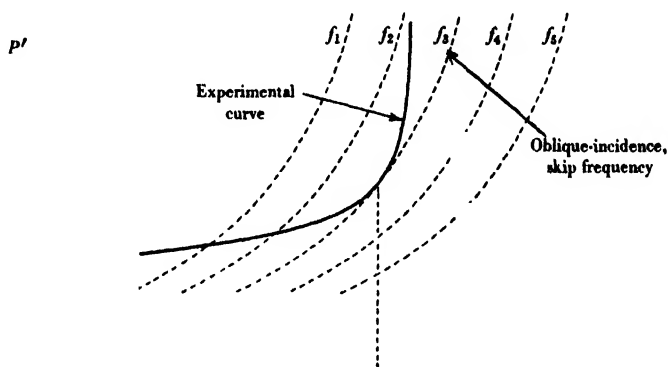


Figure 2

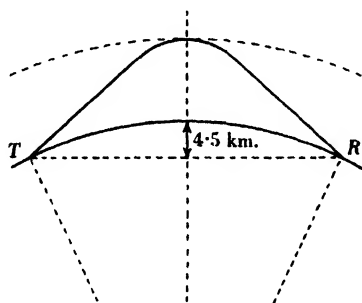


Figure 3

§ 3. EXPERIMENTAL ARRANGEMENTS

The experiments were carried out between Cambridge and Edinburgh, distant 464 km. from one another and situated on a line running approximately north and south magnetically. Pulse transmitters of conventional type were installed at the two stations, that at Cambridge being controlled by a land line from the receiving hut about 1 km. away, while that at Edinburgh was in the same room as the receiver and controlled by hand. Visual observation on a cathode-ray tube was used throughout. For normal incidence a time base synchronized to the local electric mains was employed at each end, and for oblique-incidence measurements a self-synchronizing time base⁽⁶⁾ of a type previously described was used.*

* The electric supply mains at the two places were never found to be synchronized.

The experiments were divided into two groups. The first were made before the transmitter at Edinburgh was in use, and consisted of schedules of gradually ascending frequencies transmitted from Cambridge, with 2 min. pause on each frequency, so that measurements of the echo spacing could be made at Edinburgh. Each schedule was followed by a determination of the normal-incidence $P'f$ curve at Cambridge, and the measurements were used to compare the form of the observed $P'f$ curve at oblique incidence with that calculated from the normal-incidence observations.

It was realized from these experiments that the accuracy of comparison of oblique-incidence and normal-incidence curves was impaired not only by the lack

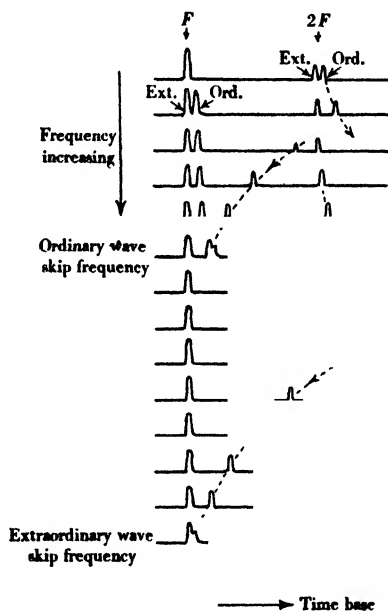


Figure 4. Echo patterns obtained at oblique incidence on a series of ascending frequencies.

The time base was synchronized to the first pulse, no ground wave being received.

of information concerning the latitude variation of ionization, but also by the time delay between the two sets of observations: a complete experiment of this type required 30 min., during which time the region- F ionization might change quite appreciably.

The subsequent experiments, in which both transmitters were used, were therefore made by a more rapid technique. The echo spacings in the oblique transmissions were not measured, but attention was confined to determining the exact frequency at which the ordinary wave disappeared. Each experiment lasted only 15 min.: during the first seven a determination was made at Cambridge of the normal-incidence $P'f$ curve, and at Edinburgh of the final penetration frequency of this curve; and during the remaining 8 min. signals having closely spaced frequencies, covering the skip frequency of the ordinary wave and each lasting

30 sec., were transmitted from Edinburgh. These were followed on the receiver at Cambridge, and the echo pattern was sketched so that the point of disappearance was accurately recorded. The type of observations obtained was as shown in figure 4.* Frequency steps of about 0.08 Mc./sec. were used, so that the critical frequency could be estimated with considerable accuracy.

By comparing the penetration frequencies for normal incidence at Cambridge and Edinburgh the variation with latitude was found. It was assumed that the form of the $P'f$ curve was the same at the mid point as at Cambridge, so that from the latitude variation the appropriate curve for the mid point could be determined. An interpolation in time (between successive runs) was also applied to eliminate as far as possible the natural variations in the ionization density. The results obtained in this way showed good agreement, and we consider that the process of interpolation is an essential part of the technique if accurate determinations are to be made.

Since the whole precision of the experiments depended on having a reliable cross calibration of frequency between the two stations, at the end of each period of experiment a test was made in which calibration frequencies, spaced by about 0.5 Mc./sec., were transmitted from one station and the receiver-dial readings were noted at the other. The dial readings were used throughout for recording frequencies.

§ 4. EXPERIMENTAL RESULTS

The experiments of the first group gave results similar to those shown in the previous paper. A typical case is reproduced in figure 5, in which the upper curves depict the penetration of the ordinary and extraordinary waves at normal incidence, and the lower the corresponding curves at oblique incidence. From the observations on the ordinary wave in the upper figure the theoretical curve for oblique incidence has been calculated; it is shown dotted in the lower figure. It is seen to agree reasonably well in form with the observed curve, and in this particular case also there is quantitative agreement between the frequencies observed and calculated. This is significant in showing that the discrepancy noted in the previous paper (of about 0.25 Mc./sec.) must be at least partly attributable to latitude variations of ionization, and could not have been relied on as the basis of any theoretical computations. These results, therefore, serve merely to confirm the previous work, and their further value depends on eliminating the uncertainty in the absolute relationship between the curves.

Of the experiments in the second group, designed solely for the comparison of critical frequencies, twenty-one gave accurate measurements of the three quantities involved, viz. the normal-incidence $P'f$ curve at Cambridge, the final penetration frequency at Edinburgh, and the skip frequency at oblique incidence. Table 1 shows the results of one of the schedules made during the night 28/29 August 1937, and the interpolation mentioned above. The region- F penetration frequencies at Cambridge and Edinburgh are given in columns 3 and 4, and the latitude variation

* This figure also illustrates the behaviour of the extraordinary wave.

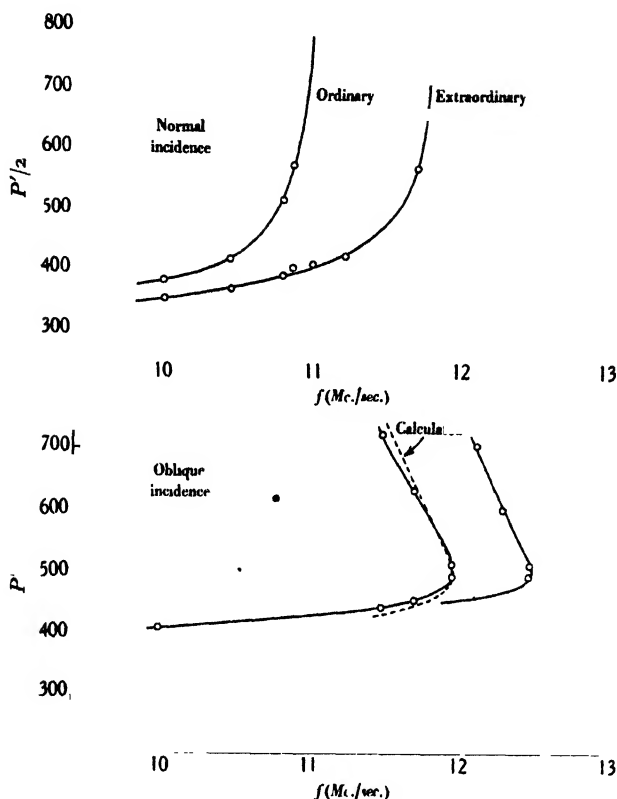


Figure 5. Normal and oblique incidence $P'f$ curves. The absolute values of P' in the oblique curves are estimated from the spacing between first and second reflections, together with the normal-incidence equivalent heights. No ground wave was received.

Table 1

Number of experiment	G.m.t.	<i>F</i> penetration (Mc./sec.)		$\frac{1}{2}$ latitude- difference (Mc./sec.)	Calculated skip frequency from Cambridge <i>Pf</i> curve (Mc./sec.)			Observed skip frequency (Mc./sec.)
		Cambridge	Edinburgh		Uncor- rected	Corrected for time	Corrected for latitude	
1	2235 2242	6·65	6·45	—0·10	7·01			
2	2250 2255	6·57	6·27	—0·15	6·92	6·97	6·87	6·88
						6·81	6·66	6·63
3	2305 2310	6·29	6·24	—0·03	6·61			
						6·56	6·53	6·47
4	2320 2326	6·15	6·13	—0·01	6·47			
						6·44	6·43	6·30
5	2335 2341	6·10	6·03	—0·03	6·31			
						6·28	6·25	6·23
6	2350 2357	6·00	5·92	—0·04	6·20			
						6·20	6·16	6·16

determined from them is given in column 5. In column 6 is given the theoretical skip frequency as calculated from the Cambridge P/f curve, and in columns 7 and 8 the same quantity after correction for time and latitude variations respectively. The resulting value is to be compared with the observed skip frequency given in the last column.

Table 2 represents the results of all the experiments after they have been subjected to calculation in this way. Ten of those shown were of the quick-schedule type, the remainder being made with a 30-min. schedule. In order to examine how closely the results of the experiments agree with the simple theory based on Martyn's theorem, we show, in column 5, the differences between the observed skip frequencies and those calculated after correction for time and latitude. In column 6 these differences are expressed as percentages of the observed frequency. The mean percentage difference is found to be 0.47 , with a probable error of ± 0.13 . The mean frequency for normal-incidence penetration is 6.86 Mc./sec., and the mean skip frequency for oblique transmission is 7.17 Mc./sec.

Table 2

Date, 1937	G.m.t.	Oblique-incidence skip frequency (Mc./sec.)		$f_{\text{cal}} - f_{\text{obs}}$ (Mc./sec.)	$\frac{f_{\text{cal}} - f_{\text{obs}}}{f_{\text{obs}}}$ %
		Observed	Calculated		
19 May	2245	7.82	7.81	-0.01	-0.13
"	2315	7.70	7.71	0.01	0.13
"	2344	7.63	7.65	0.02	0.26
20 May	0014	7.68	7.62	-0.06	-0.78
"	0112	7.43	7.44	0.01	0.13
27 May	0940	8.73	8.85	0.12	1.40
28 May	1351	7.93	7.97	0.04	0.50
"	1420	7.70	7.64	-0.06	-0.78
3 June	1425	7.55	7.42	-0.13	-1.72
10 June	2345	7.58	7.62	0.04	0.53
11 June	0055	7.30	7.43	0.13	1.78
28 Aug.	2242	6.88	6.87	-0.01	-0.14
"	2253	6.63	6.66	0.03	0.45
"	2310	6.47	6.53	0.06	0.93
"	2326	6.30	6.43	0.13	2.07
"	2341	6.23	6.25	0.02	0.32
"	2357	6.16	6.16	0.00	0.00
29 Aug.	2227	6.90	6.99	0.09	1.30
"	2242	6.73	6.81	0.08	1.20
"	2257	6.58	6.68	0.10	1.52
"	2312	6.51	6.57	0.06	0.92

We conclude from these results that there is very close agreement between the observed skip frequencies and those calculated by means of the theory for the ordinary wave, and we may express the precise relationship by stating that for a wave-frequency of about 7 Mc./sec. the oblique limiting frequency falls short of that calculated from the normal-incidence P/f curve by 0.47 ± 0.13 per cent. This value applies, of course, only to the particular ground distance and direction relative to the magnetic field of the experiments.

The extraordinary wave has not been studied so carefully. On twenty-two occasions, however, the frequency-difference between the skips of the ordinary and extraordinary waves at oblique incidence has been measured, and the average value obtained was 0.62 ± 0.013 Mc./sec. for a wave-frequency of about 7 Mc./sec. This value is very nearly the same as that observed at vertical incidence.

It will be noted that in figure 5 the separation between the ordinary and extraordinary curves at oblique incidence is less than this amount, whereas in the normal-incidence curves it is greater. This must be attributed to the slow technique used in those measurements.

§ 5. ACKNOWLEDGEMENTS

We are deeply indebted to Mr Ratcliffe for his help throughout the course of this work.

We wish also to thank the Royal Society for the loan of a pulse transmitter, and Professors Barkla and Crew for providing generous accommodation in Edinburgh University.

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NOTE ADDED IN PROOF

Since this paper was communicated, Millington has published an extension of Martyn's equivalence theorem to the case of a curved earth. The correction for curvature we have applied above is easily seen to be in agreement with his analysis for the short distance of transmission used in these experiments.

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ELECTRON-DIFFRACTION BY THE SPLIT-SHUTTER METHOD AND A NEW (BACK-REFLECTION) METHOD

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ABSTRACT. The necessity for using the grazing-incidence method when electron-diffraction is applied to the study of surface structure is emphasized, and precautions to be taken in order to obtain the maximum information from the patterns are discussed. A satisfactory method for obtaining comparison reflection patterns by the split-shutter method is described, and details of a light-tight split-shutter plate-holder are given.

In view of the limitations of the grazing-incidence method the possibility of the back-reflection of electrons is considered, and experiments are described in which high-speed electrons diffracted through angles approaching 180° are recorded photographically, the incident beam being normal to the surface of the specimen. The results obtained do not enable definite conclusions to be drawn concerning the two-dimensional or three-dimensional nature of the mechanism of diffraction involved, but development of the technique should result in a useful method applicable to those specimens which cannot at present be directly examined by electron-diffraction.

§ 1. INTRODUCTION

IN the application of electron-diffraction to the study of surface structure, the reflection or grazing-incidence method must be used, because in most cases the removal of the surface layers as a thin film suitable for use as a transmission specimen cannot be justified in view of the possibility that structural changes may be brought about during the stripping process. Thus, the stripping agent may affect the film chemically, or the breaking of the bonds between the surface layers and the matrix may cause atomic rearrangement to take place. In general it will not be possible to determine whether such change has occurred or not.

Unfortunately the reflection method is subject to certain limitations. With polycrystalline reflection specimens, a characteristic pattern will result only if there are, projecting above the general surface, crystallites sufficiently thin to transmit electrons. This condition is usually fulfilled by surfaces which have undergone mild chemical action, but severe treatment may cause the surface to become too rough to be examined at grazing incidence.

In transmission the distance from the diffracting crystal to the photographic plate is the same for all crystals, but in the grazing-incidence method there may be a variation in this length equal to the diameter of the specimen. Thus, for a given diffraction, the radius R is given by

$$R = \lambda L / d,$$

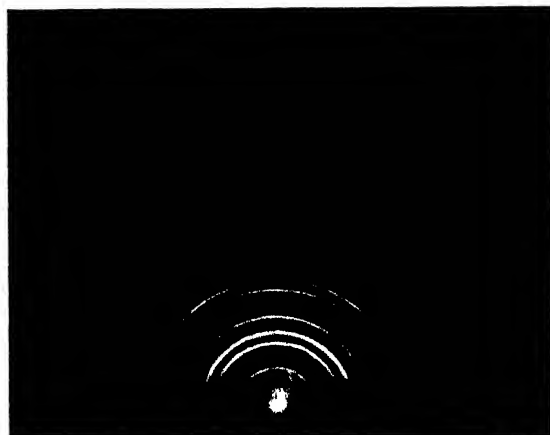


Figure 2. Fe_3O_4 .



Figure 4. Split-shutter reflection pattern: PbS and $\alpha\text{-Fe}_2\text{O}_3$.

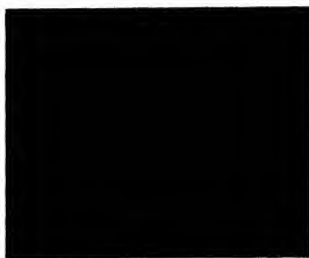


Figure 6. Back-reflection pattern from quartz single crystal.

where d is the lattice spacing, λ the electronic wave-length and L the distance from crystal to plate. Whilst d and λ are constants, L varies over a range, with a resultant line-broadening which under certain conditions may be considerable. With a camera length of 50 cm. and specimen-diameter of 3 cm. the ring-broadening due to this effect is 0.075 cm. on a ring of normal radius 1.25 cm., whilst if the specimen-size is reduced to 1 cm. the broadening is only 0.025 cm. It is for this reason that the diffractions obtained by reflection are always broader than those obtained by transmission from a comparable specimen. The narrower the rings the more accurately can their radii be determined, and therefore it is advisable to employ small specimens and as long a camera as may be convenient.

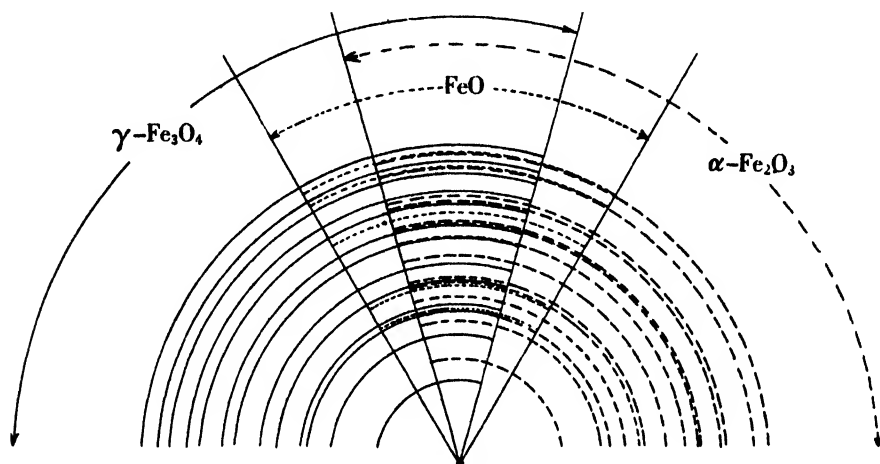


Figure 1. The relative radii of iron-oxide diffractions.

Owing to the short electronic wave-lengths employed, a large number of diffractions are recorded upon a comparatively small photographic plate, and this results in a tendency for the outermost rings to merge together. For a given structure the separation of adjacent rings is greatest for small angles of diffraction, owing to the larger differences in the corresponding lattice spacings; hence these inner rings are the most useful in deciding the structure of the specimen. This may be illustrated by reference to the oxides of iron, figure 1. In the case of Fe_3O_4 and $\alpha\text{-Fe}_2\text{O}_3$ the diffractions almost coincide, with the exception of the first two or three rings, and unless a satisfactory technique is adopted these inner rings may be cut off by the shadow-edge, or masked by the incoherent scattering around the central spot. Thus, in obtaining the pattern, figure 2, due to Fe_3O_4 , the well defined-monochromatic incident beam made possible by focusing was employed. By maintaining a high vacuum in the diffraction chamber, the background, and particularly that in the immediate neighbourhood of the central spot, was almost eliminated, whilst ring-broadening was reduced to a minimum by the combination of small specimen-size with large camera-length. These conditions, combined with low angle of incidence, enable the innermost rings to be clearly seen.

§ 2. THE SPLIT-SHUTTER METHOD

It has frequently been observed that determinations of lattice spacings made by electron-diffraction are subject to an error of the order of two per cent owing to the difficulty of determining high potentials with accuracy. Further, the important inner rings are liable to a maximum error in measurement because of the smallness of their radii, and for these reasons we have applied the split-shutter method⁽¹⁾ to reflection specimens. This method consists essentially of a comparison of two patterns, obtained under identical conditions, and afforded by the specimen and a standard reference material respectively. Whilst the split-shutter technique was easily applicable to the transmission method, some difficulty was experienced in the case of reflection because the two specimens must be coplanar. A very slight deviation from this condition is sufficient to obscure the inner rings of one of the

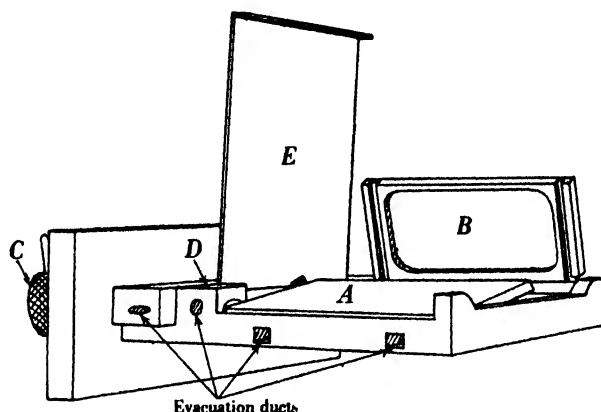


Figure 3. Light-tight split-shutter plate-holder.

patterns. Furthermore, the construction of earlier split-shutter plate-holders was such that the diffraction camera had to be used in a dark room. In our work on the oxidation of iron we have found it essential to attain the greater accuracy given by the split-shutter method, but it was necessary for the plate-holder to be light-tight. Accordingly, the plate-holder shown in figure 3 was designed. Features of the design are (i) robust construction, (ii) accurate fitting due to the fact that, once assembled, all joints can be reground without dismantling of the shutters, and (iii) evacuation of the plate-chamber, bearings, and all gas-pockets by ample ducts. The half-shutters *A* and *B* are independently operated through plane ground joints, semi-universal joints being incorporated in the head *C* and the bearing *D*. The aluminium shutter *E* was backed by the fluorescent screen and was operated by means of a third head and bevel gears. The main object of this shutter was to ensure the light-tightness of the gap between the two half-shutters *A* and *B*, but the accuracy of fit made possible by the design was such that this third shutter was hardly necessary.

§ 3. THE REFERENCE MATERIAL

In split-shutter work the main requirements of the standard reference material are that it shall (i) have a simple, known structure, (ii) be easily and quickly prepared, and (iii) give a reproducible pattern of continuous sharp rings, i.e. consist of a random distribution of fairly large crystals. In addition, for reflection work it is desirable that there shall be a number of rings of small radius to give maximum accuracy for the important diffractions, and furthermore that the reference specimen shall be easily made coplanar with the specimen under examination.

The substance which we have found to fulfil these conditions is lead sulphide, freshly precipitated from lead-nitrate solution, thoroughly washed and made up into a paste with water. The paste is applied, in the form of a thin film, to one-half of the reflection specimen by means of a camel-hair brush. By rotation of the specimen about an axis normal to its plane, either the surface to be examined or the lead sulphide can be brought into the beam without change in the angle of incidence. By this method an accuracy of one-tenth of 1 per cent in the determination of lattice spacings has been achieved. A characteristic split-shutter reflection pattern is shown in figure 4, in which rhombohedral α -Fe₂O₃ is compared with PbS.

§ 4. THE BACK-REFLECTION OF ELECTRONS

The grazing-incidence method is limited to the examination of fine wires or surfaces which are virtually plane. This precludes the investigation of a large number of surfaces which occur in practice, since violent chemical attack frequently results in the formation of irregular surfaces made up of large crystals through which the electron beam cannot penetrate. Further, just as X rays cannot be used for the determination of true surface structure because the diffractions caused by the surface layers will be swamped by those due to the underlying material, so the grazing-incidence method of electron-diffraction cannot be used for the examination of isolated areas on the specimen, as for example, corrosion spots, because the electron beam traverses a strip of the specimen and all crystals within this strip contribute to the diffraction pattern. The most obvious way of overcoming these limitations is to use normal instead of grazing incidence of the electron beam.

It is now well known that electron-diffraction from polycrystalline specimens, giving rise to well-defined rings comparatively free from background, is two-dimensional in nature. In effect the Laue condition for diffraction by the line grating parallel to the beam is almost completely relaxed, and the Laue conditions corresponding to two line gratings normal to the beam determine the diffractions which occur. A single line grating normal to the beam gives rise to cones of diffracted rays about the line grating as axis. If we consider two such line gratings defining a two-dimensional lattice, then diffractions due to the two gratings occur in the directions of intersection of the cones. Normally we record those diffractions which occur in the forward direction, yet it is clear that any two such intersecting cones will in general intersect along two directions making angles of ϕ and $(180^\circ - \phi)$

with the incident beam. Furthermore, the indices defining the diffraction occurring at $(180^\circ - \phi)$ will be the same as those defining the diffraction at ϕ . Provided the intensity of this back-reflection is sufficiently great and is not masked by any other effect, it should be possible to record by means of it patterns having essentially the same characteristics as those obtained by transmission in the forward direction.

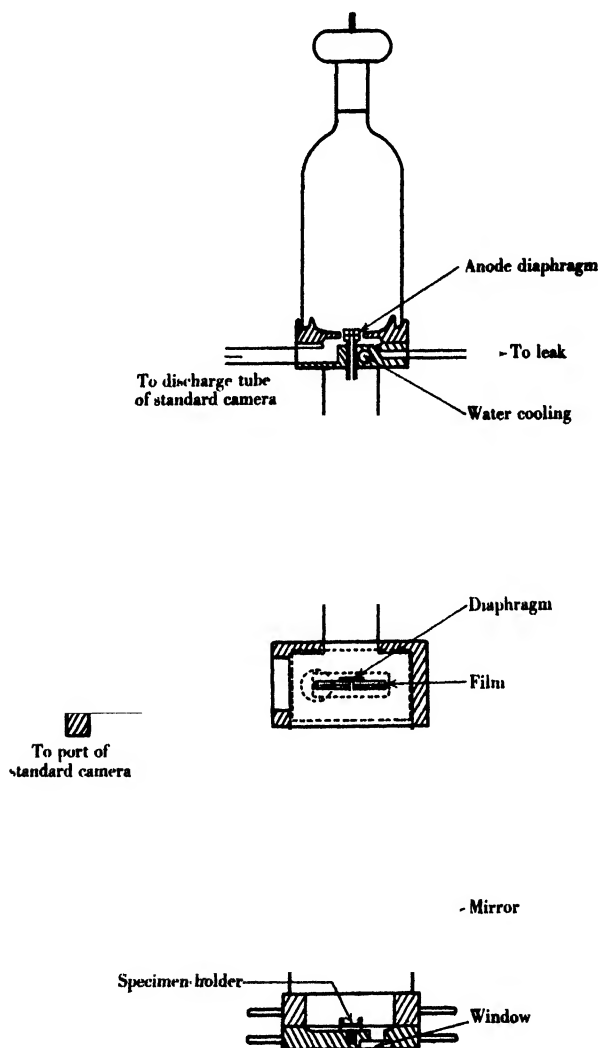


Figure 5. Back-reflection camera.

With a view to investigating the back-reflection of electrons we have constructed the simple camera shown in figure 5. The essential difference between this and the standard camera is that the relative positions of the specimen and plate-holder are reversed, and therefore provision must be made for the electrons to pass through a hole punched in the photographic film. Owing to the complications which would

be introduced by the diffracted electrons returning within the influence of the magnetic field, focusing was not employed, but the incident beam was limited by two small diaphragms 25 cm. apart. The alignment of discharge tube, diaphragms and specimen was carried out by replacing the specimen by a small fluorescent screen which could be viewed by means of a periscope. Because of the considerable distance of separation of the two diaphragms, maximum intensity of the beam could only be achieved by placing a small bar magnet just below anode-block level to deflect the beam through the lower diaphragm. This served the additional purpose of ensuring that the beam should be appreciably monochromatic.

With exposures of $\frac{1}{2}$ hr. to 1 hr. at 50 to 60 kv. and a camera-length of 30 cm., specimens of (i) a fairly thick layer of polished Aquadag colloidal graphite, (ii) gold foil, and (iii) Armco iron rubbed on no. 00 emery paper, all failed to yield a diffraction pattern, although blackening of the photographic film was observed. Experiments in which one-half of the film was covered with thin black paper proved conclusively that this blackening was not due to X rays. Moreover, when the film was reversed, the celluloid base acted as a shield, completely preventing blackening of the emulsion, which could not, therefore, be attributed to light emitted by the specimen under the action of electrons. It having thus been shown that electrons scattered through angles approaching 180° could be detected photographically, further specimens were examined. On the two-dimensional theory all the specimens so far discussed should have yielded ring patterns, and it is possible that the spreading of the diffracted electrons over such a comparatively large area would result in the intensity being too small for detection in view of the relatively intense background.

An Armco iron specimen, so deeply etched that it would not give a diffraction pattern by the grazing-incidence method, afforded an irregular pattern of from 20 to 30 spots of weak intensity. Further, with the electron beam at normal incidence on a natural (112) face of a rather imperfect quartz crystal, the spot pattern shown in figure 6 was obtained, the exposure being 1 hr. at 45 kv.

These spot patterns cannot be satisfactorily analysed because of the uncertainty which exists as to the exact centre of the pattern, falling as it does somewhere within the hole punched in the film, and therefore it would be imprudent to advance any definite theory as to the mechanism of diffraction involved. The fact that patterns are not always obtained would suggest that the diffraction is three-dimensional, but it would in that case be difficult to explain why five well-defined spots were given by a quartz single crystal with a monochromatic electron beam. Further, as has been mentioned above, the failure to obtain ring patterns from specimens known to consist of random distributions of crystals may well be due to the reduction in intensity caused by the spreading of the diffracted electrons over a relatively large area, and this view is supported by the fact that, whilst the five spots from a quartz single crystal were fairly intense, the more numerous spots yielded by a microcrystalline Armco specimen were very much weaker. It is possible that the Laue condition for the row of atoms parallel to the incident beam is neither completely relaxed nor fully operative, in which case the patterns would

have some of the characteristics of both two-dimensional and three-dimensional diffraction.

Whatever the true explanation of these patterns may be, we feel that development of the technique will result in a useful method of investigation, applicable to those specimens which cannot at present be directly examined by electron-diffraction.

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AN INVESTIGATION OF COSMIC-RAY SHOWERS PRODUCED UNDER THIRTY METRES OF CLAY

By J. D. CRAWSHAW, M.Sc.

Communicated by Prof. P. M. S. Blackett, 6 May 1938. Read in title 24 June 1938

ABSTRACT. The vertical intensity of the cosmic radiation and of the cosmic-ray shower-intensity have been measured at ground level and at a station 30 m. below the surface, and the ratio of these two quantities has been shown to be nearly the same at the two levels. A transition curve in lead has been obtained at the Underground station and its shape differs widely from the typical curve obtained at sea level. After a sharp initial rise, the shower-rate remains stationary for thickness of lead up to 8.8 cm., in contrast to the rapid decrease which occurs after the maximum at sea level. The curves obtained underground are shown to be very similar to those obtained by Drigo at sea level under about 2 m. of masonry.

§ 1. INTRODUCTION

THE work described by Follett and Crawshaw⁽¹⁾ on the comparison of both the vertical intensity and the shower intensity of cosmic radiation at ground level and under 30 m. of clay has been continued. The experiments were carried out in the Underground station at Holborn.

In the earlier work, the ratio of the vertical intensity to the maximum shower-rate was shown to be approximately equal at the two levels. The object of the present experiment was to confirm this interesting and rather unexpected result and to obtain a reliable transition curve for showers from lead at the lower level.

§ 2. EXPERIMENTAL ARRANGEMENT

The vertical intensity and the shower-rates were observed by means of the coincident discharges of five Geiger-Müller counters. With five counters the casual-coincidence rate is so small that a correction for it may be omitted.

The counters were 30 cm. long and 1.6 cm. in internal diameter, and were filled at a pressure of 20 cm. of mercury with a mixture of three parts of argon to one part of air. The anode of each counter was a tungsten wire, and the cathode consisted of a cylinder of oxidized copper foil, the whole being sealed into a glass container. The potential applied to each counter was 50 v. above its starting potential. The recording apparatus used is shown in figure 1 and is similar in design to that described by Barasch⁽²⁾.

For successful quintuple recording, the smallest output pulse resulting from discharges in all five counters must be greater than the largest pulse resulting from discharges in all but one of the counters. A quintuple coincidence was recorded when a 6-v. impulse was applied simultaneously to each of the five grids. No false

quintuple was observed when a 120-v. impulse was applied simultaneously to any four of the five grids; from this result, it was assumed that a movement of the telephone counter corresponded to a coincident discharge of the five counters. The leads from the anodes of the counters to the grids of the valves were made as short as possible and were screened so as to prevent any mutual-induction effects. Each pentode was enclosed in a screening box.

The apparatus was set up in a laboratory with a thin roof at ground level, five counters being used one above another, and measurements were made of the vertical intensity of the cosmic rays. The axes of these counters were horizontal and the plane containing the axes was vertical.

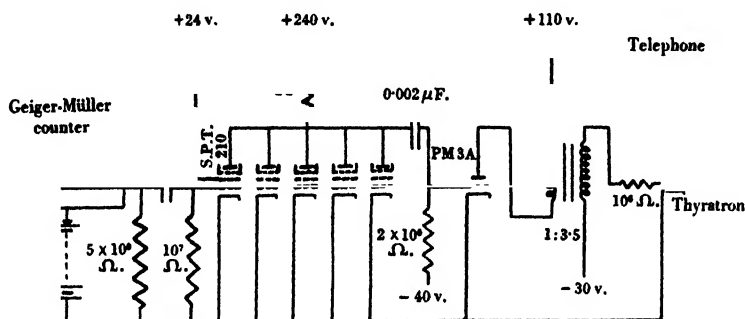


Figure 1. Coincidence recording circuit.

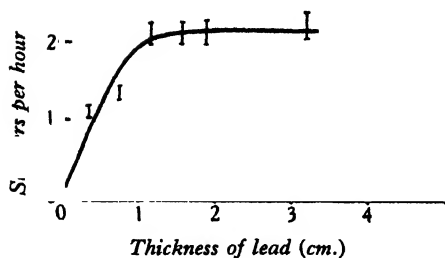


Figure 2. Transition curve for sheet A. I, probable error of the determination.

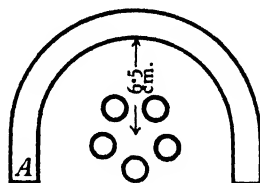


Figure 2 A. Arrangement of counters.

For the shower-rate determination, the counters were arranged as shown in figure 2A; their axes were horizontal and formed the apices of a regular pentagon. Such an arrangement requires at least three ionizing particles to discharge it, and thus the showers observed consist of at least three such rays. Observations were made with and without lead over the counters. The lead sheets shown in figure 2A were bent into a nearly semicircular shape and had a thickness of 1.6 cm., since this value gives the maximum shower-rate at ground level.

The apparatus was then taken down to a disused platform in Holborn tube station and was housed in a galvanized iron shed. The platform is about 30 m. below ground level, and above it are strata of different kinds of clay whose mean specific gravity is about 2, giving a total thickness of absorber equivalent to about 60 m. of

water. Measurements of the vertical intensity and the transition curves for lead were obtained. As a check on the apparatus, a redetermination of the vertical intensity at ground level agreed with the former value.

§ 3. EXPERIMENTAL RESULTS

Table 1. Vertical intensity

	Total count	Time	Rate per hour
Ground level	1189	4 h. 30 m.	264 ± 5.2
Underground level	454	32 h. 55 m.	13.8 ± 0.45
Ratio of intensities 19.1 ± 0.7			

Table 2. Shower-rates with a hemicylinder of lead, 1.6 cm. thick above the counters. Figure 2

	Total count	Time	Rate per hour
Ground level	331	7 h. 40 m.	43.2 ± 1.6
Underground level	107	49 h. 40 m.	2.15 ± 0.14
Ratio of shower-rates 20.0 ± 1.5			

For the measurement of vertical intensity the counters were equally spaced, the axes of the two outer counters being 12.5 cm. apart. In the pentagonal formation the axes of the counters were 2.7 cm. apart. The shower-rate for the thickness of lead here used decreases with increasing depth below the surface at about the same rate as the primary radiation, in agreement with the former results of Follett and Crawshaw⁽¹⁾.

With the arrangement shown in figure 2A the transition curve up to 3 cm. of lead was measured underground, figure 2. The shape differs markedly from that of the usual air-lead curve at sea level; see, for instance, curve *A* of figure 4, which shows some results obtained by Drigo⁽⁴⁾. The shower-rate underground rises with increasing thicknesses of lead up to 1.2 cm. and then remains stationary, while at sea level there is a marked maximum at about 1.6 cm.

To extend the transition curve to greater thicknesses of lead a special frame was constructed to carry the lead sheets, which were bent into circular arcs subtending an angle of 108° at the axis of the bottom counter; this second disposition of lead is represented by *B* in figure 3A. A transition curve, figure 3, was then obtained for thicknesses of lead up to 8.8 cm. The shower-rate is less than with the semicircular sheets, but the commencement of the stationary value occurs at about the same thickness of lead. There is no rapid decrease of shower-rate with increasing thickness of lead up to 8.8 cm.

It is seen that the reduction of the area of lead sheet leads to about a proportional reduction of the shower-intensity. For the case of the hemicylindrical lead sheets, the maximum rate is about 2.15 per hour, whereas in the case of the sheets subtending an angle of 108° with the axis of the bottom counter the maximum rate is about 1.40 per hour. The zenith-angle distribution of the cosmic-ray intensity has already

been determined by Follett and Crawshaw⁽¹⁾ at this depth below ground level, and the intensity at angles from the zenith greater than 54° is much too small to explain the observed decrease of intensity unless the harder horizontal rays are more active in producing showers than the softer vertical radiation. The probable explanation is that the showers are so diffuse and contain so many scattered particles that the chance that one will be recorded is almost independent of whether the lead absorber, in which it is produced, is at the side or over the top of the counters. In addition, the average size of a shower probably increases with the area of the lead absorber. This must happen if, as is probable, many of the incident rays coming from the roof of the tunnel are already associated in showers.

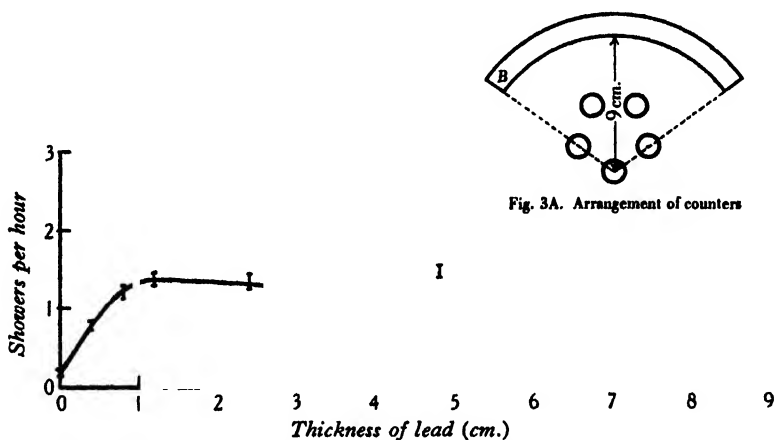


Figure 3. Transition curve for sheet B. I, probable error of the determination.

Experiments have been made with lead sheets placed under the counters, but within the limits of experimental error the effect of such sheets is negligible; this shows that no appreciable number of shower particles are projected upwards.

Auger and Rosenberg⁽³⁾ have obtained similar transition curves at depths of 30 and 75 m. water equivalent, but they found that the stationary value of the shower-rate was reached with a considerably smaller thickness of lead than in our experiments in the Underground station. Moreover, they noticed that this thickness decreased with increasing depths below the surface. Perhaps the difference may be due to the difference in the arrangement of counters.

§ 4. DISCUSSION OF RESULTS

Drigo⁽⁴⁾ has obtained transition curves at ground level with increasing thicknesses of light-absorbing material above the lead and counters, figure 4. The remarkable features of his results are that the greater the thickness of absorbing material, the less pronounced is the maximum of the curve, and that the curve C obtained with a thickness of light-absorbing material equivalent to 2.7 m. of water is similar to that found at the Underground station, where there is a thickness of 30 m. of clay above the apparatus.

This type of curve thus appears to be characteristic of a transition to lead from a

compact mass of material composed of elements of low atomic number. Its shape seems independent of the thickness of material above the lead and counters, provided that this thickness is greater than that equivalent to about 2 m. of water.

On account of the difference between the curves of the transition from air to lead and from masonry to lead, care has to be exercised in comparing the ratio of the shower rates at ground level and at a position 30 m. below this level. In the above

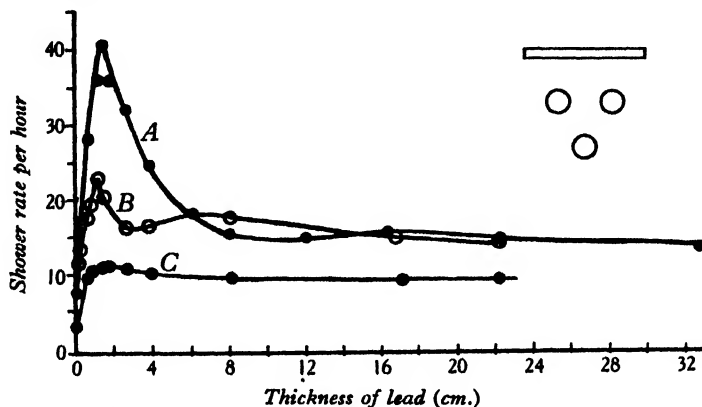


Figure 4. Curves plotted from results of A. Drigo (1935). A, filtered by 20 g./cm² of light material; B, filtered by 20 g./cm² of light material and 88 g./cm² of lead; C, filtered by 270 g./cm² of light material.

experiments, the ratio of the shower-rate to the vertical intensity has been shown to be the same at the two levels, but from a consideration of the curves in figure 4 the shower-rate at sea level, for a thickness of 1.6 cm. of lead, is several times greater for an air-lead transition than for a masonry-lead transition. Thus the ratio of shower-rate to vertical intensity must be actually greater underground than under a few metres of masonry at sea level. This is a rather surprising result, and suggests that either the size or the number of showers produced by the penetrating component must increase as the radiation becomes more penetrating, and so probably more energetic, as a result of filtration.

§ 5. ACKNOWLEDGEMENT

The author wishes to thank Prof. Blackett for suggesting this experiment and for his guidance and assistance during its progress. He wishes also to thank Dr H. J. J. Braddick and Dr S. W. Watson for their suggestions and assistance; the London Passenger Transport Board for permission to use the Holborn tube station; and lastly the staff at the station for assistance in many ways.

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THE FREQUENCY OF VIBRATION OF MOLECULES IN LIQUIDS AND ITS RELATION TO VISCOSITY

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ABSTRACT. An expression is found for the variation, with temperature, of the average frequency of vibration of a molecule in a liquid. The absolute frequency is calculated approximately and is used in Andrade's expression for the viscosity of a liquid at the melting point, namely, $\eta = \frac{4}{3} \cdot \nu m / \sigma$, to obtain an expression for the variation of viscosity with temperature. The absolute value of the viscosity is calculated approximately. The internal pressures of several monatomic liquids have been calculated.

§ 1. INTRODUCTION

ANDRADE⁽¹⁾ has developed an expression for the viscosity of a liquid at the melting point, namely

$$\eta = \frac{4}{3} \frac{\nu m}{\sigma} \quad \dots\dots(1).$$

In this expression m is the molecular weight of the substance, σ the mean distance between the centres of the molecules and ν the average frequency of vibration of the molecules. The value of the frequency calculated in this way has been shown, for monatomic substances, to be practically identical with that calculated from Lindemann's well-known expression

$$\nu = 2.8 \times 10^{12} \sqrt{\frac{T_s}{MV}} \quad \dots\dots(2).$$

Andrade has applied the expression in the above form to the melting point only. In order to account for the variation of viscosity with temperature he assumes that, for the transference of momentum, the molecules must possess a certain mutual potential energy. The number of molecules possessing this energy will be governed by the Boltzmann distribution formula. From this he arrives at the expression

$$\eta v^{\frac{1}{2}} = A e^{E/Tv} \quad \dots\dots(3)$$

for the variation of viscosity with temperature. In arriving at the latter expression he assumes that the average frequency of vibration is independent of temperature. This assumption was made partly because of the difficulty of finding a satisfactory expression for the change of frequency with temperature, and partly because the

assumption of a constant frequency gave a more exact representation of the observed values.

Lindemann's expression for the frequency of vibration of an atom at the melting point is based on the assumption that at the melting point the amplitude of vibration of the atoms is approximately equal to their mean distance apart. There is no necessary justification for assuming that the amplitude is actually equal to the distance apart of the atoms. The same expression would be obtained by assuming it to bear a constant ratio, for various substances, to the atomic diameter. The arbitrary numerical constant would thereby be altered, but as this is obtained by comparison with the experimentally determined values of the frequency the general applicability of the formula would not be affected. It is obvious that if the expression is applied to a liquid above the melting point, it would indicate an increase of frequency with rise of temperature, because \sqrt{T} increases much more rapidly than $V^{\frac{1}{3}}$. Such an increase would, of course, preclude the application of equation (1) to liquids above the melting point without further assumptions.

§ 2. THE CHANGE OF FREQUENCY WITH TEMPERATURE

On general grounds, there is reason to expect that the average frequency of the atoms of a liquid would decrease with rise of temperature. In a solid the frequency is of the order of 10^{12} per sec., whereas in a gas under ordinary conditions the collision frequency is of the order of 10^9 per sec. Regarding a liquid as an intermediate state between a solid and a gas, we should expect a gradual lowering of the average frequency with rise of temperature.

It is proposed to assume that the movement of a liquid molecule is essentially that of a small sphere vibrating in an envelope slightly larger than itself. Taking the simplest possible analogy of a piston moving in a cylinder, in which the radius of the piston is r , the unoccupied length of the cylinder h and the velocity of the piston c , the frequency for a complete oscillation is given by

$$\nu = \frac{\pi r^2 c}{2\pi r^2 h} \text{ or } \frac{c}{2h} \quad \dots\dots(4).$$

In like manner, the time for a complete oscillation of a liquid molecule can be considered to be the time required by the molecule to sweep out a volume equal to twice the unoccupied volume of its envelope. If V_0 is the specific volume of a liquid at a low temperature, we can consider that the area of a molecule is proportional to $(MV_0/N)^{\frac{2}{3}}$, where M is the molecular weight, N is Avogadro's number, and V_0 is considered to be constant. If at some higher temperature the specific volume is v , then we can consider that the unoccupied portion will be $(v - V_0)$, or the ratio of the unoccupied portion to the occupied portion will be $(v - V_0)/V_0$. The volume of a single molecule can be taken as proportional to MV_0/N , so that the unoccupied volume associated with a single molecule will be

$$\frac{MV_0}{N} \times \frac{v - V_0}{V_0}.$$

Let c be the average velocity of a molecule at the temperature considered. On the above analogy we can expect the frequency to be some simple function of

$$\frac{(MV_0/N)^{\frac{1}{2}} c}{2 (MV_0/N) (v - V_0)/V_0},$$

or we can write
$$\nu = \frac{Kc}{2 (MV_0/N)^{\frac{1}{2}} (v - V_0)/V_0} \quad \dots\dots(5).$$

K should be a small numerical quantity differing from unity because the assumptions are only approximate. V_0 will be considered to be the specific volume at the lowest temperature in the range of temperature over which the measurements are applicable.

The velocity c of a molecule is proportional to $\sqrt{T/M}$, where T is the absolute temperature and M is the molecular weight. We can write, therefore,

$$\nu = \frac{K'}{2 (MV_0/N)^{\frac{1}{2}} (v - V_0)/V_0} \sqrt{\frac{T}{M}} \quad \dots\dots(6).$$

If now we consider a liquid at its melting point and assume that at the melting point the free space bears a constant ratio to the volume of the molecule for various substances, which is a more generalized form of Lindemann's assumption, the above expression gives for the frequency at the melting point

$$\nu_s \propto \sqrt{\frac{T_s}{M} \cdot \frac{1}{(MV_0/N)^{\frac{1}{2}}}} \quad \dots\dots(7),$$

which is identical with Lindemann's expression. At higher temperatures the frequency will decrease so that at a temperature t the frequency is given by

$$\nu_t = \nu_s \frac{v_s - V_0}{v_t - V_0} \sqrt{\frac{T}{T_s}}. \quad \dots\dots(8)$$

$v_t - V_0$ increases more rapidly than \sqrt{T} .

§3. THE VISCOSITY OF A LIQUID

If now we insert the above expression for the frequency into Andrade's expression, equation (1), for the viscosity of liquid at the melting point, we obtain

$$\eta = \frac{4}{3} \frac{K'}{(MV_0/N)^{\frac{1}{2}} (v - V_0)/V_0} \sqrt{\frac{T}{M} \cdot \frac{M}{\sigma}} \quad \dots\dots(9).$$

Regarding V_0 as a constant and writing σ as proportional to $v^{\frac{1}{2}}$, we could derive the expression for the variation of viscosity of a liquid with temperature, in which M is constant, as

$$\frac{\eta v^{\frac{1}{2}}}{\sqrt{T}} = \frac{B}{v - V_0}, \text{ where } B \text{ is a constant} \quad \dots\dots(10).$$

The calculation of the free space from this equation should enable us to obtain approximately the absolute value of the frequency and the absolute value of the viscosity.

In the following tables, the equation

$$\frac{\eta v^{\frac{1}{2}}}{\sqrt{T}} = \frac{B}{v - V_0} \quad \dots\dots(11),$$

which involves two unknowns, B and V_0 , is applied to monatomic substances. A comparison is shown of the differences between the calculated and observed values obtained by its use and those from the use of Andrade's expression, equation (3).

Unfortunately the range of experimental data in this class of substance is still very meagre, and the technical difficulties in connexion with the measurement of the viscosity at the relevant temperatures makes it almost impossible to reach the accuracy obtainable with organic substances at ordinary temperatures.

Table 1. Gallium. Spells⁽²⁾

Temp. ° K.	η_{obs}	Volume cm ³	$\frac{\eta v^{\frac{1}{3}}}{\sqrt{T}}$	B $v - V_0$ (cal.)	Difference between calculated and observed values (per cent)	
					Equation (11)	Equation (3)
303	0.02027	0.9917	0.021167	0.021242	+7.0	—
325.9	0.01894	0.9944	0.021042	0.021063	+2.1	+3.9
373.0	0.01609	1.0000	0.028331	0.02833	0.0	+0.6
422.0	0.01406	1.0060	0.026864	0.02673	-2.0	-1.7
473.0	0.01258	1.0120	0.025808	0.02563	-3.0	-3.4
574.0	0.01029	1.0230	0.024333	0.02435	+0.5	-2.2
675.0	0.00882	1.0345	0.023433	0.02351	+2.3	-0.1
773.0	0.008127	1.0453	0.022967	0.02297	+0.1	-1.6
873.0	0.007637	1.0560	0.022632	0.02258	-2.0	-3.0
1079.0	0.006524	1.0778	0.02035	0.02035	0.0	+1.3
1283.0	0.005915	1.0998	0.021705	0.021675	-1.9	+3.3
1373.0	0.00578	1.1097	0.021615	0.021553	-3.2	+2.7

$(v - V_0)$ at 373° K. is 0.02515.

The differences with gallium over a range of temperature of 1000° are of the same order with the two expressions but are, if anything, more at random with equation (11).

$(v - V_0)$ at 303° K. calculated from first two readings is 0.0229.

Table 2. Potassium. Chiong⁽³⁾

Temp. ° K.	η_{obs}	Volume cm ³	$\frac{\eta v^{\frac{1}{3}}}{\sqrt{T}}$	B $v - V_0$ (cal.)	Difference between calculated and observed values (per cent)	
					Equation (11)	Equation (3)
337.2	0.005535	0.9894	0.022996	0.022897	-3.3	—
340.0	0.005256	0.9903	0.022842	0.022841	0.0	+0.3
340.9	0.005230	0.9906	0.022825	0.022823	0.0	+0.3
352.4	0.004930	0.9940	0.022630	0.022631	0.0	-0.3
372.5	0.004540	1.0000	0.022353	0.022353	0.0	0.0
392.6	0.004188	1.0060	0.022118	0.022127	+0.4	-0.4
428.5	0.003707	1.0167	0.021807	0.021813	+0.3	-0.6
448.5	0.003530	1.0227	0.021680	0.021678	-0.1	+0.4
480.7	0.003249	1.0323	0.021497	0.021497	0.0	+0.6
555.5	0.002750	1.0546	0.021196	0.021196	0.0	-0.2
625.5	0.002457	1.0756	0.021007	0.021007	0.0	0.0

The volume has been calculated from the expression given in the Landolt-Börnstein tables as follows:

$$V_t = V_{372.5} [1 + 0.03299 (t - 372.5)]. \quad v - V_0 \text{ at } 372.5^\circ \text{ K. is } 0.0565.$$

The agreement with the author's expression is strikingly good in the case of this substance.

$v - V_0$ at 337.2° K. calculated from values at 337.2° K. and 352.4° K. is 0.0330.

Table 3. Sodium. Chiong⁽³⁾

Temp. ° K.	η_{obs}	Volume cm ³	$\frac{\eta v^{\frac{1}{3}}}{\sqrt{T}}$	$\frac{B}{v - V_0}$ (cal.)	Difference between calculated and observed values (per cent)	
					Equation (11)	Equation (3)
371.0	0.007264	0.9988	0.033772	0.033697	-2.1	—
372.6	0.007142	0.9994	0.033697	0.033637	-1.7	—
375.4	0.006856	1.0000	0.033539	0.033580	+1.1	—
393.4	0.006170	1.0051	0.033116	0.033153	+1.2	+0.3
428.4	0.005322	1.0146	0.032585	0.032581	-0.2	-0.3
432.1	0.005225	1.0158	0.032526	0.032523	-0.1	-0.1
446.7	0.004942	1.0198	0.032354	0.032347	-0.3	-0.2
456.4	0.004760	1.0225	0.032244	0.032242	-0.1	-0.2
479.7	0.004431	1.0290	0.032043	0.032024	-1.0	-0.7
491.0	0.004239	1.0321	0.031933	0.031933	0.0	0.0
562.0	0.003506	1.0519	0.031504	0.031506	+0.1	-0.3
628.0	0.003015	1.0703	0.031231	0.031249	+1.4	+0.7

$(v - V_0)$ at 375.4° K. is 0.0377.

The volume has been calculated from the expression given in the Landolt-Börnstein tables, namely

$$V_t = V_{375.4} [1 + 0.03278 (t - 375.4)].$$

$(v - V_0)$ at 371° K. calculated from values at 371.0° K. and 393.4° K. is 0.0290.

Table 4. Tin. Stott⁽⁴⁾

Temp. ° K.	η_{obs}	Volume cm ³	$\frac{\eta v^{\frac{1}{3}}}{\sqrt{T}}$	$\frac{B}{v - V_0}$ (cal.)	Difference per cent
513	0.0191	1.0000	0.03843	0.03843	0.0
573	0.0167	1.0054	0.03697	0.03690	-1.0
673	0.0138	1.0144	0.03535	0.03529	-1.2
773	0.0118	1.0235	0.03428	0.03428	0.0
873	0.0105	1.0326	0.03359	0.03359	0.0
973	0.00945	1.0416	0.03307	0.03310	+1.0
1073	0.0087	1.0507	0.03270	0.03272	+0.8

The volume has been calculated from the expression

$$V_t = V_{513} [1 + 0.04905 (t - 513)],$$

based on the results of Lewis⁽⁵⁾.

$v - V_0$ at 513° K. is 0.0242.

Table 5. Bromine. Thorpe and Rodger⁽⁶⁾

Temp. ° K.	η_{obs}	Volume cm ³	$\frac{\eta v^{\frac{1}{3}}}{\sqrt{T}}$	$\frac{B}{v - V_0}$ (cal.)	Difference per cent
273	0.012575	1.0000	0.037610	0.037590	-0.3
283	0.01109	1.0108	0.036613	0.036613	0.0
293	0.009935	1.0219	0.035845	0.035843	-0.1
303	0.008985	1.0335	0.035218	0.035207	-0.2
313	0.00817	1.0454	0.034685	0.034685	0.0
323	0.00747	1.0576	0.034235	0.034250	+0.3

$(v - V_0)$ at 273° K. is 0.0733.

Table 6. Mercury

Temp. ° K.	η_{obs}	Volume cm ³	$\frac{\eta v^{\frac{1}{3}}}{\sqrt{T}}$	$\frac{B}{v - V_0}$ (cal.)	Difference per cent
253	0.0186	0.9963	0.031171	0.031169	-0.2
273	0.0170	1.0000	0.031029	0.031029	0.0
293	0.0157	1.0037	0.030919	0.030919	0.0
323	0.0141	1.0091	0.03787	0.03795	+1.0
373	0.0122	1.0183	0.03636	0.03646	+1.6
473	0.0102	1.0368	0.03475	0.03470	-1.0

$(v - V_0)$ at 273° K. is 0.0309.

These tables show that equation (11) follows the experimental values with an error not much greater than the probable experimental uncertainty.

§4. THE FREE SPACE AT THE MELTING POINT

On the basis of Lindemann's assumption, the free space at the melting point should bear, approximately, a constant ratio to the total volume for various substances. Of the substances given above, bromine will be shown to fit in more satisfactorily with the organic substances and will be discussed with them.

Table 7 tabulates the values of the free space calculated for the remaining elements and gives the values computed for the melting points.

Table 7

	Temp. ° C.	$v - V_0$	Melting point ° C.	(i) $v - V_0$ at melting point	(ii) $v - V_0$ at melting point
Mercury	0	0.0309	-39	0.0237	0.0237
Tin	240	0.0242	232	0.0232	0.0232
Gallium	100	0.0252	30	0.0170	0.0224
Sodium	103	0.0384	97	0.0366	0.0291
Potassium	100	0.0565	62	0.0446	0.0320

In the neighbourhood of the melting point, the viscosities of gallium, sodium and potassium show definite anomalies whether calculated by Andrade's equation (3) or by equation (11). The last column gives the free space for these substances

calculated from the experimental values immediately above the melting point. While the values in column (i) can hardly be called approximately constant, those in column (ii) are much more so. The very high compressibilities of sodium and potassium in the solid form would suggest that in these elements the atoms themselves are compressible. If that is the case, some portion of their very large coefficients of expansion may be due to an actual increase in the volume of the atom as the substance expands. The expansion of the free space would, therefore, be less than that calculated from the ordinary coefficient of expansion. Such an anomaly would account for the higher value for these substances. In the method of approach of Lindemann and Andrade this difficulty would not appear. A more extended range of data is necessary to establish the constancy or otherwise of the free space at the melting point, calculated in this way. In the meantime the values can be said to be of the same order and, in the case of mercury, tin and gallium, approximately constant.

§5. CALCULATION OF THE ABSOLUTE FREQUENCY

It is now possible to attempt the calculation of the absolute frequency from equation (5).

The values for sodium at 103°C. , which is not far from the melting point, are $(v - V_0)/V_0 = 0.0384$, $M = 23$, $N = 6.06 \times 10^{23}$ and $\rho = 0.93$; $V_0 = 1/\rho$; c is obtained from the known kinetic energy of a molecule at 0°C. , namely 5.62×10^{-14} ergs, and the mass of the sodium atom, namely $23 \times 1.64 \times 10^{-24}$ gram, by the formula

$$c = \sqrt{\frac{2 \times 5.62 \times 10^{-14} \times 376}{23 \times 1.64 \times 10^{-24} \times 273}} \text{ cm./sec.}$$

Taking K as unity, this gives the absolute frequency of the sodium atom as 2.42×10^{13} . Andrade's value for sodium is 4.6×10^{12} . The value is, therefore, five times too great. This might be considered too great a numerical factor, even after allowance for the approximate nature of the initial assumptions. It will be shown that for the organic substances the numerical factor is much lower and that its large value in the case of the elementary substances is probably connected with their very small molecular volume.

§6. ORGANIC SUBSTANCES

There is little doubt that organic substances, with falling temperature, tend to undergo some sort of loose association of the molecules, varying according to the nature of the substance. Such an association would involve an alteration in the effective molecular weight. It might be expected, therefore, that the simple expression (11) would apply less satisfactorily to organic substances over any extended range of temperatures. It still remains, however, approximately true for those liquids which are ordinarily considered to be unassociated. A more exact agreement can, of course, be obtained by introducing an arbitrary coefficient and writing

$$\frac{\eta v^{\frac{1}{2}}}{\sqrt{T}} = \frac{B}{(v - V_0)^n} \quad \dots\dots(12).$$

The value of n for unassociated substances is very close to unity. This type of expression has been discussed by the author in earlier papers^(7,8,9). The value of the free space, calculated over a small range of temperature from equation (11), is not very different from that obtained from the expression

$$\eta = \frac{B}{v - \bar{V}_0} \quad \dots\dots(13).$$

It was shown by the author⁽⁹⁾ that the specific volume of a liquid can be accurately represented by the expression

$$\pi_0 e^{c''/Tv} = \frac{RT}{v - \bar{V}_0},$$

where $\pi_0 e^{c''/Tv}$ is considered to be the internal pressure of the liquid. It was also shown that if the molecular weight changed owing to any loose association of molecules, it would be expected to change so that

$$M = M_0 e^{c'/Tv}.$$

Substituting for $1/(v - \bar{V}_0)$ the quantity $\pi_0 e^{c''/Tv}/RT$, and representing any change in the molecular weight as covered by the expression $M = M_0 e^{c'/Tv}$, we obtain the following possible expressions for the viscosity of a liquid, in which the molecular weight is not necessarily constant.

$$\begin{aligned} \eta v^{\frac{1}{2}} &= \frac{K_0 e^{c'/Tv}}{v - \bar{V}_0} \quad \dots\dots(14) \\ &= \frac{K_0 e^{c'/Tv} \pi_0 e^{c''/Tv}}{RT} \\ &= \frac{K e^{c'/Tv}}{T} \end{aligned}$$

or $\eta v^{\frac{1}{2}} \sqrt{T} = K e^{c'/Tv} \quad \dots\dots(15),$

this latter equation involving only two unknowns. The use of these expressions will be shown as applied to diethyl ketone for which Thorpe and Rodger⁽⁶⁾ give the expression for the relation between temperature and volume as

$$V_t = V_0 [1 + 0.0211534t + 0.051884t^2 + 0.083202t^3] \quad \dots\dots(16),$$

an expression involving four unknowns.

The equation $\pi_0 e^{c''/Tv} = \frac{T}{v - \bar{V}_0} \quad \dots\dots(17)$

is applied to the volumes calculated from the equation (16). Equation (17) involves only three unknowns. The calculated values are obtained from the values of the constants, which unfortunately have to be obtained by the method of trial and error, thus: $V_0 = 0.9000$, $c'' = 418.1$, $\pi_0 = 587.4$.

It is obvious that an expression of this type represents the specific volume of a liquid with considerable accuracy.

Table 8. Diethyl ketone

Temp. ° C.	Volume cm. ³	$v - V_0$	$\frac{T}{v - V_0}$	$\pi_0 c''/Tv$	Difference per cent
0	1.0000	0.1000	2730	2717	-0.5
10	1.0117	0.1117	2535	2531	-0.2
20	1.0238	0.1238	2367	2367	0.0
30	1.0363	0.1363	2223	2225	+0.1
40	1.0493	0.1493	2096	2098	+0.1
50	1.0627	0.1627	1985	1986	0.0
60	1.0766	0.1766	1885	1885	0.0
70	1.0909	0.1909	1795	1796	0.0
80	1.1059	0.2059	1714	1714	0.0
90	1.1213	0.2213	1640	1641	0.0
100	1.1373	0.2373	1572	1574	+0.1

If now we take the value of V_0 as 0.9000, which has been determined independently of viscosity data, and insert it in equation (14), we have an equation which involves only two unknowns, namely K_0 and c' . This expression gives a very accurate representation of the experimental values. The values of the constants are: $c' = 160.0$, $K_0 = 0.031995$, $V_0 = 0.9000$.

Table 9. Diethyl ketone

Temp. ° C.	$\eta_{\text{obs.}}$	η_{calc}
0	0.00595	0.00593
10	0.00525	0.00524
20	0.00466	0.00467
30	0.004195	0.004194
40	0.003795	0.003792
50	0.003445	0.003445
60	0.00315	0.00315
70	0.00289	0.00289
80	0.002655	0.002654
90	0.00245	0.00245
100	0.00226	0.00227

It will be seen that the experimental values are almost exactly reproduced.

By eliminating $(v - V_0)$ we obtain the equation

$$\eta v^{\frac{1}{2}} \sqrt{T} = K e^{c/Tv},$$

where $c = c' + c'' = 578.1$ and $K = K_0 \times \pi_0 = 0.1172$. In the following tables this equation is applied to several liquids, and a comparison is made of the differences between the observed and calculated values obtained by its use with those by the use of Andrade's expression, equation (3). The values of $(v - V_0)$, calculated from the approximate equation

$$\eta v^{\frac{1}{2}} \sqrt{T} = \frac{B}{v - V_0} \quad \dots\dots(18),$$

along with the divergences from the observed values, are also given. From the approximate value of $(v - V_0)$ thus obtained the absolute frequency has been cal-

culated in the manner illustrated for sodium. The absolute viscosity is then obtained from equation (1). The observed value is shown in brackets.

Table 10. Diethyl ketone

Temp. ° C.	η_{obs}	$\eta v^{\frac{1}{2}} \sqrt{T}$	$K\epsilon c/Tv$	Difference per cent	From Andrade's formula	$\frac{B}{v - V_0}$
0	0.00595	0.0983	0.0974	-0.9	-0.4	+1.6
10	0.00525	0.0886	0.0883	-0.3	-0.2	+0.3
20	0.00466	0.0805	0.0805	0.0	-0.1	0.0
30	0.004195	0.0739	0.0739	0.0	0.0	-0.8
40	0.003795	0.0682	0.0682	0.0	-0.2	-1.0
50	0.003445	0.0632	0.0632	0.0	-0.3	-1.1
60	0.00315	0.0589	0.0588	-0.2	-0.4	-1.1
70	0.00289	0.0551	0.0550	0.2	-0.3	-0.7
80	0.002655	0.0516	0.0516	0.0	0.0	0.0
90	0.00245	0.0485	0.0485	0.0	+0.4	+0.5
100	0.00226	0.0456	0.0458	+0.4	+0.8	+1.5

$c = 578.1$; $K = 0.1172$; $(v - V_0)$ at $0^\circ \text{C.} = 0.0701$; $v_0 = 3.36 \times 10^{12}$; $\eta_0 = 0.01056$ (0.00595).

Table 11. Octane

Temp. ° C.	η_{obs}	Volume cm ³	$\eta v^{\frac{1}{2}} \sqrt{T}$	$K\epsilon c/Tv$	Difference per cent	From Andrade's formula	$\frac{B}{v - V_0}$
0	0.00703	1.0000	0.1161	0.1152	-0.8	-0.4	7.0
10	0.006125	1.0119	0.1035	0.1030	-0.5	-0.3	2.0
20	0.00538	1.0238	0.09282	0.09282	0.0	0.0	0.0
30	0.004785	1.0360	0.08427	0.08428	0.0	-0.2	-1.5
40	0.00428	1.0485	0.07690	0.07697	+0.1	-0.2	-2.0
50	0.003855	1.0612	0.07068	0.07070	0.0	-0.2	-2.1
60	0.003495	1.0745	0.06531	0.06518	-0.2	-0.6	-2.1
70	0.00318	1.0882	0.06058	0.06042	-0.3	-0.6	-1.7
80	0.002905	1.1025	0.05638	0.05625	-0.2	-0.5	-1.3
90	0.00266	1.1174	0.05257	0.05257	0.0	-0.3	-0.6
100	0.002445	1.1331	0.04922	0.04922	0.0	0.0	0.0
110	0.002255	1.1496	0.04624	0.04626	0.0	0.0	+0.4
120	0.002075	1.1670	0.04332	0.04358	+0.6	+0.7	+1.4

$c = 655.6$; $K = 0.1044$; $(v - V_0)$ at $0^\circ \text{C.} = 0.0543$; $v_0 = 3.52 \times 10^{12}$; $\eta_0 = 0.0137$ (0.00703).

Table 12. Carbon tetrachloride

Temp. ° C.	η_{obs}	Volume cm ³	$\eta v^{\frac{1}{2}} \sqrt{T}$	$K\epsilon c/Tv$	Difference per cent	From Andrade's formula	$\frac{B}{v - V_0}$
0	0.01346	1.0000	0.2223	0.2192	-1.4	-1.4	+3.5
10	0.01133	1.0122	0.1914	0.1914	0.0	0.0	0.0
20	0.00969	1.0245	0.1672	0.1681	+0.5	+0.6	-1.1
30	0.00842	1.0371	0.1484	0.1494	+0.7	+0.7	-1.2
40	0.00738	1.0502	0.1328	0.1337	+0.7	+0.7	-1.4
50	0.00654	1.0636	0.1200	0.1205	+0.4	+0.5	-0.6
60	0.005835	1.0776	0.1092	0.1092	0.0	0.0	0.0
70	0.00524	1.0932	0.1000	0.0995	-0.5	-0.8	+0.1

$c = 793.1$; $K = 0.1199$; $(v - V_0)$ at $0^\circ \text{C.} = 0.0494$; $v_0 = 3.75 \times 10^{12}$; $\eta_0 = 0.0217$ (0.0135).

Table 13 gives the absolute frequency and the absolute viscosity calculated for a large number of liquids at temperatures approximately 20° below their boiling points. The free space was obtained by means of equation (18) from observed values at two temperatures 20° and 10° below the boiling point. In calculating the absolute value, K was taken as unity. The last column gives the numerical ratio of the calculated value to the observed value. It is practically constant for this class of substances, which includes bromine and nitrogen peroxide, and is much smaller than the ratio for the metals. The organic substances are distinguished from the metals by their much larger atomic volumes as well as for their greater free space. It might be expected that the error due to the approximations made would become greater as the scale is reduced; in the gaseous state the time between collisions is long compared to the time of the actual collision, whereas in a liquid a molecule is practically in a state of continual collision; the actual nature of the collision, which is relatively unimportant in a gas, becomes one of the determining factors in a liquid. A considerable numerical correction is therefore to be expected. In the case of the organic substances the value actually required is certainly not unreasonable.

Table 13

Substance	Temp. ° C.	$\nu \times 10^{-12}$	$\eta_{calc.}$	$\eta_{obs.}$	Ratio
Pentane	10	2.00	0.00550	0.00256	2.15
Heptane	70	1.50	0.00516	0.00253	2.04
Octane	100	1.22	0.00456	0.00244	1.87
Propyl chloride	20	2.17	0.00691	0.00352	1.97
Propyl bromide	50	1.55	0.00773	0.00388	2.00
Propyl iodide	80	1.24	0.00830	0.00420	1.99
Carbon tetrachloride	50	1.99	0.01230	0.00654	1.88
Chloroform	40	1.83	0.00910	0.00465	1.96
Propylene bromide	120	1.56	0.01194	0.00535	2.23
Benzene	60	2.63	0.00836	0.00391	2.14
Ethyl benzene	110	1.53	0.00586	0.00282	2.08
Ethyl sulphide	70	1.60	0.00543	0.00279	1.95
Carbon bisulphide	20	2.36	0.00847	0.00367	2.30
Methyl propyl ether	10	2.13	0.00624	0.00277	2.25
Dipropyl ether	60	1.64	0.00589	0.00277	2.13
Diethyl ether	10	2.02	0.00592	0.00259	2.28
Propyl acetate	80	1.78	0.00673	0.00304	2.21
Methyl formate	10	2.65	0.00745	0.00384	1.94
Nitrogen peroxide	0	2.66	0.01140	0.00528	2.16
Bromine	0	5.75	0.02910	0.0126	2.30
Potassium	62	16.9	0.0336	0.0056	6.00
Sodium	97	31.9	0.0466	0.0075	6.20
Mercury	0	10.9	0.1557	0.0170	9.00
Gallium	30	28.5	0.1697	0.0204	8.32
Tin	240	22.2	0.1900	0.0191	10.0

§7. THE INTERNAL PRESSURE OF THE LIQUIDS

It is of interest to calculate the internal pressures Π of the elements on the assumption that they are given approximately by the expression

$$\Pi = \frac{RT}{(v - V_0)M/\rho}.$$

Table 13 sets out the values obtained in atmospheres. The approximate value of their coefficients of cubical expansion are also given.

Table 14

Substance	Temp. ° C.	Π	α
Tin	240	104,600	0.0310
Gallium	100	108,000	0.0311
Mercury	0	50,500	0.0318
Sodium	100	43,000	0.0328
Potassium	64	18,600	0.0330
Bromine	0	12,200	0.0310

Except in the case of potassium, the coefficients of expansion are approximately inversely proportional to the internal pressures. There is an obvious relation between the internal pressure of a liquid and its viscosity, as both are largely governed by the free space.

§8. ACKNOWLEDGEMENTS

In conclusion, I wish to express my thanks to Dr F. W. G. White, Professor of Physics at Canterbury College, and to Mr C. J. Banwell, M.Sc., for helpful criticism and encouragement.

NOTE ADDED IN PROOF

My attention has been drawn to the recent papers by Eyring in the *Journal of Chemical Physics* on the physical properties of liquids, to which no reference is made in this paper. Unfortunately the journal is not available in Christchurch and I was unaware of the contents of Eyring's papers when I was preparing mine. Any conclusions, therefore, arrived at in this paper are independent of those arrived at by Eyring.

I have now obtained copies of Eyring's papers but I find that his method of approach is different from mine, though he makes use of the terms "free volume" and "internal pressure" in his discussion. The expression "free space or volume" as understood in the present paper has been defined both in it and my earlier papers^(7, 8, 9) and evidence has been brought forward to show that it corresponds to the free-volume term in Van der Waals's equation. In calculating the internal pressure of a liquid Van der Waals has been followed in that only attractive static forces have been considered. It is of interest, however, to note that the values of the intrinsic cohesive pressures for potassium, sodium and mercury, given above, are of the same order and bear a similar relationship to one another as do those given by Richards for the same substances in a paper published in the discussion by the Faraday Society on Cohesion and Related Problems, November 1927. The following table sets out the values obtained by the author and by Richards:

Substance	Richards	Author
Potassium	15,300	18,600
Sodium	33,000	43,000
Mercury	41,300	50,500

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THE RELATION BETWEEN IONOSPHERIC TRANSMISSION PHENOMENA AT OBLIQUE INCIDENCE AND THOSE AT VERTICAL INCIDENCE

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ABSTRACT. This paper gives a modification for a curved earth of Martyn's theorems, relating oblique-incidence ionospheric phenomena with observed conditions at vertical incidence. The theorems in their modified form are shown to hold, as regards both equivalent frequency and absorption, for a relatively thin layer above the earth's surface. It is assumed that the ionic density has the same vertical gradient everywhere between the transmitter and receiver, and that the effect of the earth's magnetic field can be neglected. Methods of allowing approximately for these two factors are discussed. A set of transmission curves is derived, with which the skip frequency at any given distance from the transmitter can be obtained graphically from an observed $P'f$ curve at vertical incidence. Similar curves are given for deducing equivalent heights and angles of elevation at oblique incidence, together with graphs of the maximum receivable frequency at extreme distances and the maximum distance of single-hop transmission, as functions of the height of the layer. The application of the theorem is thus reduced, for the benefit of engineers, to a simple technique of using a number of standard curves in conjunction with a given $P'f$ curve.

§ 1. INTRODUCTION

THE problem of determining the characteristics of long-distance transmission through the ionosphere, as regards the maximum usable frequency and the absorption en route, is a very important one from the point of view of the engineer who has to allocate wave-lengths for any projected service. It would be a difficult and tedious business to make ionospheric measurements for a comprehensive set of conditions at oblique incidence, and it would be very useful if the required data could be deduced from observations made at vertical incidence by the standard $P'f$ technique.

Martyn⁽¹⁾ has shown that a simple relation does actually exist between results taken at vertical incidence and those which would be obtained at oblique incidence, provided that three assumptions are made: (1) that the gradient of electronic density is everywhere vertical and similar along the oblique path, (2) that the earth's magnetic field is negligible, and (3) that the earth is flat. The first assumption is roughly satisfied if, for instance, the whole of the transmission path lies in a region of bright daylight, or if the transmission, regarded as a single hop, is referred to the ionospheric conditions at the mid point of the path where the reflection takes place. The second assumption is approximately justified at short distances, but at longer

distances it leads to values of maximum usable frequency for the extraordinary ray which are too big. The third assumption also leads to values which are considerably too big for long distances.

It is difficult to assess the error due to the neglect of the earth's magnetic field, owing to the complexity of the analysis involved in the magneto-ionic theory. It is, however, possible to examine the effect of the earth's curvature in some detail and to express the result as a modification of Martyn's theorem. In this paper the general ray theory of a curved earth and ionosphere is developed in a form suitable for the discussion of transmission at very oblique incidence, in which the ray may leave the earth almost tangentially. The results obtained are presented in a set of curves for use in practical cases, and some discussion is given of their application to long-distance transmission problems.

§ 2. GENERAL RAY THEORY FOR A CURVED EARTH

Figure 1 represents a ray leaving a transmitter T at an angle of elevation α , and arriving at a receiver R at a distance y along the surface of the earth. If ϕ is the angular distance, and r_0 is the radius of the earth, $y = r_0 \phi$. PQ is an element ds

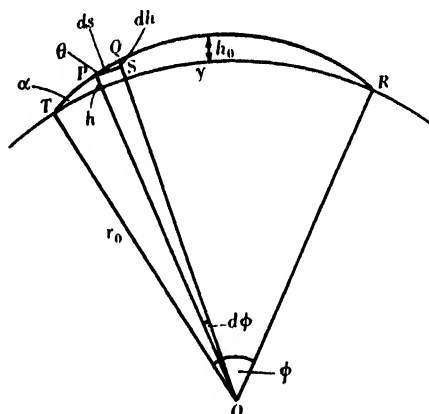


Figure 1. Geometry of ray-path for a curved earth.

of the ray path, corresponding to a height h above the surface of the earth and to an angular distance $d\phi$. In the figure, SQ represents dh and $PS = (r_0 + h) d\phi$, while the angle of elevation QPS at P is θ . We therefore have

$$(r_0 + h) d\phi = ds \cos \theta$$

and

$$y = \int r_0 d\phi = \int \frac{r_0}{r_0 + h} ds \cos \theta \quad \dots (2.1).$$

But if the refractive index of the ionosphere at P is μ , and is taken as unity on the earth at T , the fundamental ray equation for the curved earth is

$$\mu (r_0 + h) \cos \theta = r_0 \cos \alpha \quad \dots (2.2),$$

so that equation (2.1) may be written

$$y = \int \left(\frac{r_0}{r_0 + h} \right)^2 \cos \alpha \frac{ds}{\mu}.$$

Now if h_0 is the height to which the ray penetrates at its apex, it follows that y lies between the values

$$\cos \alpha \int \frac{ds}{\mu} \quad \text{and} \quad \left(\frac{r_0}{r_0 + h_0} \right)^2 \cos \alpha \int \frac{ds}{\mu}.$$

But $\int \frac{ds}{\mu}$ is the equivalent path P'_{ob} given by ct , where t is the time taken for the ray to pass from T to R , and c is the velocity of the ray in free space. We may therefore write

$$y = \left(1 - \gamma \frac{h_0}{r_0} \right) P'_{ob} \cos \alpha \quad \dots\dots(2.3),$$

where γ is of the order of unity.

This relation shows that whatever the law of the gradient in the ionosphere and however long the ray path may be, the flat-earth relation $y = P'_{ob} \cos \alpha$ is only slightly modified, provided that h_0/r_0 is very small compared with unity. Strictly speaking γ can only be determined if we know the relation between the electronic density N and the height h . To study further the form of P'_{ob} , we must make use of the well-known relation

$$1 - \mu^2 = \frac{Ne^2}{\pi m f^2} \quad \dots\dots(2.4),$$

where e and m are the electronic charge and mass, and f is the frequency of the wave. N is a function of the height h , so that it is convenient to write equation (2.4) as

$$1 - \mu^2 = \frac{g(h)}{f^2} \quad \dots\dots(2.5),$$

where

$$g(h) = \frac{Ne^2}{\pi m} \quad \dots\dots(2.6).$$

Now from figure 1, $ds = dh/\sin \theta$, so that

$$P'_{ob} = \int \frac{ds}{\mu} = 2 \int_0^{h_0} \frac{dh}{\mu \sin \theta} \quad \dots\dots(2.7).$$

But if $h/r_0 \ll 1$, we have from equation (2.2)

$$\sin^2 \theta \approx 1 - \left(1 - \frac{2h}{r_0} \right) \frac{\cos^2 \alpha}{\mu^2},$$

i.e.

$$\mu^2 \sin^2 \theta = \sin^2 \alpha + \frac{2h}{r_0} \cos^2 \alpha - (1 - \mu^2).$$

Using equation (2.5) and writing f_{ob} for the frequency used at oblique incidence, we have

$$\mu^2 \sin^2 \theta = \sin^2 \alpha + \frac{2h}{r_0} \cos^2 \alpha - \frac{g(h)}{f_{ob}^2} \quad \dots\dots(2.8).$$

At the apex of the path where $h=h_0$ and $\theta=0$, and μ from equation (2.2) is given by $r_0 \cos \alpha / (r_0 + h_0)$, we have from equation (2.8)

$$\frac{g(h_0)}{f_{ob}^2} = \sin^2 \alpha + \frac{2h_0}{r_0} \cos^2 \alpha \quad \dots (2.9).$$

Now if a frequency f at vertical incidence reaches a height h_0 where $\mu=0$, we have

$$g(h_0) = f^2 \quad \dots (2.10).$$

Corresponding to a frequency f at vertical incidence we may therefore define an equivalent frequency f_{ob} at oblique incidence, such that at the apex of its path it reaches the same height h_0 , and from equations (2.9) and (2.10) we see that f_{ob} and f are connected by the relation

$$f_{ob}^2 = \frac{f^2}{\sin^2 \alpha + \frac{2h_0}{r_0} \cos^2 \alpha},$$

$$\text{i.e.} \quad f_{ob} = \frac{f \operatorname{cosec} \alpha}{\sqrt{(1 + 2h_0 r_0^{-1} \cot^2 \alpha)}} \quad \dots (2.11).$$

Equation (2.8) may now be written

$$\mu \sin \theta = \frac{\sqrt{(1 + 2h_0 r_0^{-1} \cot^2 \alpha)}}{f \operatorname{cosec} \alpha} \sqrt{\left\{ \frac{f^2 (1 + 2h_0 r_0^{-1} \cot^2 \alpha)}{(1 + 2h_0 r_0^{-1} \cot^2 \alpha)} - g(h) \right\}}.$$

Putting this value into equation (2.7), we get

$$P'_{ob} = \frac{2f \operatorname{cosec} \alpha}{\sqrt{(1 + 2h_0 r_0^{-1} \cot^2 \alpha)}} \int_0^{h_0} \frac{dh}{\sqrt{\left\{ \frac{f^2 (1 + 2h_0 r_0^{-1} \cot^2 \alpha)}{(1 + 2h_0 r_0^{-1} \cot^2 \alpha)} - g(h) \right\}}} \quad \dots (2.12).$$

If P' is the equivalent path at vertical incidence for the frequency f , we have, by putting $\alpha=90^\circ$ in equation (2.12),

$$P' = 2f \int_0^{h_0} \frac{dh}{\sqrt{f^2 - g(h)}} \quad \dots (2.13),$$

and for a flat earth at oblique incidence we have, by putting $r_0 = \infty$ in equation (2.12),

$$P'_{ob} = 2f \operatorname{cosec} \alpha \int_0^{h_0} \frac{dh}{\sqrt{f^2 - g(h)}},$$

i.e., from equation (2.13),

$$P'_{ob} = P' \operatorname{cosec} \alpha.$$

This is Martyn's theorem relating the equivalent path P'_{ob} for oblique incidence with initial angle of elevation α for a frequency f_{ob} , given from equation (2.11) by $f \operatorname{cosec} \alpha$, with the equivalent path P' at vertical incidence for a frequency f .

We cannot accurately interpret the general expression for the curved earth given in equation (2.12) unless we know the form of $g(h)$ as a function of h , i.e. unless we know the nature of the gradient of electronic density, whereas for the flat-earth case the theorem holds independently of any assumed form of the gradient. But from the form of the integrand in equation (2.12) we can see that the integral in

the expression for P'_{ob} is greater than the corresponding integral in the expression for P' in equation (2.13), so that we know that

$$P'_{ob} > P' \operatorname{cosec} \alpha / \sqrt{(1 + 2h_0 r_0^{-1} \cot^2 \alpha)}.$$

Now if we exclude very small values of α and only consider values for which $h_0 r_0^{-1} \cot^2 \alpha \ll 1$, i.e. for which $\tan \alpha \gg \sqrt{(h_0/r_0)}$, it can be seen that in general the integral in equation (2.12) is only slightly greater than the corresponding integral in equation (2.13). Near the apex of the ray, where the denominator in the integral approaches zero, we also approach the condition where h becomes h_0 , and the denominator approaches $\sqrt{\{f^2 - g(h)\}}$ as in the integral in equation (2.13). By assuming a layer of the form $g(h) = ah - bh^2$ having a maximum density at a height $a^2/2b$, and by choosing a and b so that $g(h_0)$ is equal to f and $a^2/2b$ is only slightly greater than h_0 , we can show that in a typical case in which the ray is near to the escape condition, P'_{ob} is only slightly greater than $P' \operatorname{cosec} \alpha$. Thus in general it appears that when $h_0 r_0^{-1} \cot^2 \alpha \ll 1$, the relation $P'_{ob} = P' \operatorname{cosec} \alpha$ is still very nearly true, while equations (2.3) and (2.11) give approximately $y = P'_{ob} \cos \alpha$ and $f_{ob} = f \operatorname{cosec} \alpha$ respectively, so that $\tan \alpha = P'/y$.

These relations are formally the same as for a flat earth, but it must be remembered that they have been shown to hold even when the ray travels to a long distance, so that y is measured round the surface of the earth, and the angle α , considered as the initial angle of elevation on the curved earth, may be markedly different from the corresponding angle in the flat earth case.

Martyn has also given an analogous theorem relating the absorption at oblique incidence for the frequency f_{ob} with that at vertical incidence for the frequency f . If the absorption occurring over the length ds of the path is represented by the factor $\exp[-\kappa ds]$, the absorption coefficient is given by

$$\kappa = \frac{\nu}{2c\mu} \frac{g(h)}{f_{ob}^2} \quad \dots\dots(2.14),$$

where $g(h)$ is given by equation (2.6) as before, and ν is the collisional frequency of the electrons and is a function of h .

$$\text{We have} \quad \kappa ds = \frac{\nu}{2c\mu} \frac{g(h)}{f_{ob}^2} \frac{dh}{\sin \theta},$$

$$\text{so that} \quad \int_{\text{oblique}} \kappa ds = 2 \int_0^{h_0} \frac{\nu}{2c\mu} \frac{g(h)}{f_{ob}^2} \frac{dh}{\sin \theta}.$$

Again substituting from equation (2.8) for $\mu \sin \theta$, and from equation (2.11) for f_{ob} , we get

$$\int_{\text{oblique}} \kappa ds = \frac{\sin \alpha \sqrt{(1 + 2h_0 r_0^{-1} \cot^2 \alpha)}}{cf} \int_0^{h_0} \frac{\nu g(h) dh}{\sqrt{\left\{ \frac{f^2 (1 + 2h_0 r_0^{-1} \cot^2 \alpha)}{(1 + 2h_0 r_0^{-1} \cot^2 \alpha)} - g(h) \right\}}}$$

It is obvious that with the same limitations the absorption theorem still holds, namely

$$\int_{\text{oblique for } f_{ob}} \kappa ds = \sin \alpha \int_{\text{vertical for } f} \kappa ds.$$

If we write $\exp [j - \kappa ds]$ as a reflection coefficient ρ , then

$$\frac{[\log \rho]_{\text{oblique for } f_{\text{ob}}}}{[\log \rho]_{\text{vertical for } f}} = \sin \alpha \quad \dots\dots(2.15).$$

The condition $\tan \alpha \gg \sqrt{(h_0/r_0)}$ which we have assumed implies a serious limitation to the application of the theorem to long-distance transmission at very oblique incidence. This limitation has arisen because we have considered the ionosphere to extend down to the surface of the earth, whereas actually we know that it exists as well-defined layers of thickness small compared with their height above the ground. Suppose, therefore, that we consider a layer whose lower edge is at a height H above the ground, and in which the maximum density occurs at a height h_0 above this edge, then a ray leaving the earth tangentially will enter the layer with an angle of elevation α for which $\tan \alpha = \sqrt{(2H/r_0)}$. As this is large in comparison with $\sqrt{(h_0/r_0)}$, our condition is always satisfied for such a layer.

§3. ANALYSIS FOR A THIN LAYER ABOVE THE EARTH'S SURFACE

In figure 2 the ray enters the layer at T' and leaves it again at R' , and the straight-line portions TT' and RR' of the path between the earth and the layer can be determined in terms of the height of the layer and the angle of elevation α at which

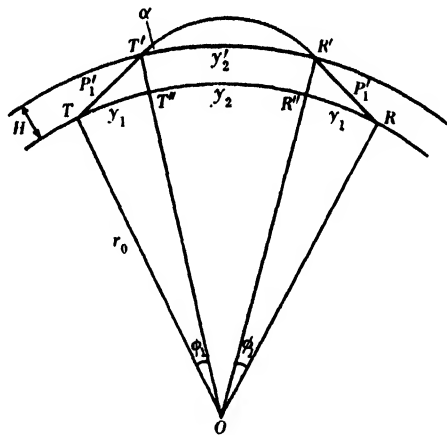


Figure 2. Geometry of ray-path for a curved earth when the lower edge of the ionosphere is at a height H .

the ray enters the layer. Corresponding to the arc $T'R'$ of the circle of radius $r_0 + H$, which we will call y_2' , is an arc $T''R''$ on the surface of the earth. Calling this arc y_2 , and each of the arcs TT'' and $R''R$, y_1 , we have

$$y = 2y_1 + y_2 \quad \dots\dots(3.1).$$

If we call each of the paths TT' and $R'R$, P_1' , and the equivalent path in the layer P_2' , then the total equivalent path P'_{ob} is now given by

$$P'_{\text{ob}} = 2P_1' + P_2' \quad \dots\dots(3.2).$$

If ϕ_1 is the angle subtended at the centre of the earth, O , by y_1 , then from $\Delta TOT'$

$$\frac{r_0 + H}{r_0} = \frac{\cos(\alpha - \phi_1)}{\cos \alpha}.$$

Therefore

$$1 + \frac{H}{r_0} = \cos \phi_1 [1 + \tan \alpha \tan \phi_1] \\ = \left(1 - \frac{\phi_1^2}{2}\right) (1 + \phi_1 \tan \alpha),$$

whence

$$\phi_1^2 - 2 \tan \alpha \cdot \phi_1 + \frac{2H}{r_0} = 0$$

and

$$y_1 = r_0 \phi_1 = r_0 \tan \alpha - r_0 \sqrt{(\tan^2 \alpha - 2H/r_0)} \quad \dots\dots(3.3).$$

This approximation is close enough, and gives the limits $\tan \alpha = \sqrt{2H/r_0}$ and $y_1 = \sqrt{2r_0 H}$ when $\phi_1 = \alpha$, and the ray leaves the earth tangentially. Also for large values of $\tan \alpha$, y_1 approximates to $H/\tan \alpha$, as it should.

Inspection now shows that the analysis simplifies considerably, if we assume that on entering the layer the ray suffers a slight diminution of angle given by changing α to α' , where

$$\tan \alpha' = \tan \alpha / (1 + H/r_0) \quad \dots\dots(3.4).$$

In justification of this procedure, we notice that the change produced in α is only of the order of error involved in determining y_1 as above, and that the ratio of α/α' , which has a maximum value of $(1 + H/r_0)$ when α is small, decreases to unity as α approaches 90° at vertical incidence. Applying the curved-earth theory as developed in the previous section, we now have

$$P_2' = y_2' \sec \alpha' = (P' - 2H) \operatorname{cosec} \alpha' \quad \dots\dots(3.5),$$

where P' , referring to the frequency f at vertical incidence, is still measured from the earth's surface. The frequency f_{0b} can still be written, to the accuracy to which we are justified in working, as

$$f_{0b} = f \operatorname{cosec} \alpha \quad \dots\dots(3.6).$$

Now

$$y_2 = \frac{y_2'}{1 + H/r_0} = \frac{P' - 2H}{(1 + H/r_0) \tan \alpha'}, \quad \text{from equation (3.5),}$$

i.e. from equation (3.4)

$$y_2 = (P' - 2H) \cot \alpha \quad \dots\dots(3.7).$$

The assumption in equation (3.4) was designed to remove the $1 + H/r_0$ term from y_2 , and to give it in the form in equation (3.7). Now from equations (3.1) and (3.3)

$$y - y_2 = 2r_0 \tan \alpha - 2r_0 \sqrt{(\tan^2 \alpha - 2H/r_0)},$$

i.e.

$$(y - y_2)^2 - 4(y - y_2) r_0 \tan \alpha = -8r_0 H \quad \dots\dots(3.8).$$

By analogy with the flat-earth case it is convenient to write

$$\tan \alpha = \frac{kP'}{y} \quad \dots\dots(3.9),$$

where k is a modification factor to be determined. If further we write

$$P' = 2mH \quad \dots\dots(3.10),$$

i.e.
$$m = \frac{h'}{H},$$

where h' is the equivalent height for the frequency f at vertical incidence, so that m is a parameter expressing the penetration of the ray into the layer, then equation (3.7) may be written

$$y_2 = \frac{m-1}{km} y \quad \dots\dots(3.11),$$

and
$$y - y_2 = 2y_1 = \left(\frac{km - m + 1}{km} \right) y \quad \dots\dots(3.12).$$

With this substitution equation (3.8) reduces down to

$$y = \left[\frac{km}{km - m + 1} \right] \sqrt{\{8r_0 H m (k-1)\}} \quad \dots\dots(3.13),$$

$\sqrt{\{8r_0 H\}}$ represents the distance to which a ray leaving the earth tangentially would go if it were reflected as from a mirror at a height H above the earth, i.e. as from the layer without any penetration, for which $m = 1$. This suggests that we should write

$$l = \frac{y}{\sqrt{\{8r_0 H\}}} \quad \dots\dots(3.14),$$

so that equation (3.13) becomes

$$l = \left(\frac{km}{km - m + 1} \right) \sqrt{\{m (k-1)\}} \quad \dots\dots(3.15).$$

Values of l greater than unity imply that there must be some penetration into the layer if the ray is to travel to the assumed distance y , and for a given value of l which is greater than unity, there exists a minimum possible value of m which corresponds to the ray that leaves the earth tangentially. Corresponding to this value of m there will be a maximum possible value of k . From equations (3.9) and (3.10) we have

$$\tan \alpha = \frac{2kmH}{y} = \frac{km}{l} \sqrt{\frac{H}{2r_0}}$$

by substitution from equation (3.14).

By writing k_{\max} and m_{\min} for the tangential ray, we get

$$\tan \alpha = \sqrt{\frac{2H}{r_0}} = \frac{k_{\max} m_{\min}}{l} \sqrt{\frac{H}{2r_0}}$$

and
$$k_{\max} m_{\min} = 2l.$$

Combining this with equation (3.15) we get

$$m_{\min} = 2l - 1, \quad \text{where } l > 1$$

and
$$k_{\max} = \frac{2l}{2l - 1}, \quad \text{where } l > 1.$$

When $l < 1$ the maximum value of k occurs when $m = 1$ and $k = 1 + l^2$. The maximum possible value of k is thus 2 when $l = 1$ and $m = 1$, it being remembered that by definition m cannot be less than unity.

Strictly speaking equation (3.15) has to be solved for k for assumed values of l and m , but in practice l is calculated for assumed values of k and m , and then k is plotted as a function of l for a series of values of m , as shown in figure 3. Since equation (3.15) only contains k , l , and m , one set of curves suffices to represent all combinations of P' , H and y . The curves are drawn to represent the limiting

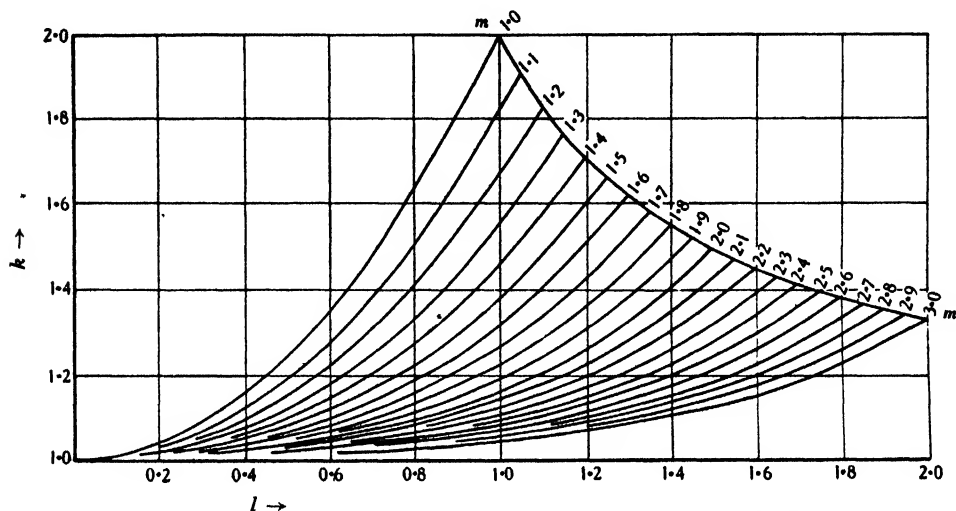


Figure 3. Curves showing k as a function of l for various values of m .

conditions that $m > 1$, and that when $l > 1$, $m > 2l - 1$, and they are arbitrarily cut off at $m = 3$, as the parts retained cover most practical conditions.

From the general shape of the curves we can see at a glance when the factor k exceeds any arbitrary value chosen as the point at which Martyn's theorem needs modification. For assumed values of H and y , l is determined from equation (3.14), and from a given value of P' on the $P'f$ curve at vertical incidence, m is given by equation (3.10). For the values of l and m so obtained, k is read off the curves, and $\tan \alpha$ is then derived from equation (3.9). The equivalent frequency f_{ob} is then obtained from equation (3.6). In this way the value of f_{ob} for each point on the $P'f$ curve can be obtained, but as it is a somewhat lengthy process we seek a simple graphical method for converting the values of f into the required values of f_{ob} .

§ 4. CONSTRUCTION OF TRANSMISSION CURVES

It is convenient to adopt the technique suggested by Smith⁽²⁾ in a recent research paper published by the National Bureau of Standards. We notice that equation (3.6) expresses f_{ob} by its equivalent vertical-incidence value multiplied by cosec α , so that it should be possible by the use of a logarithmic scale to devise a sliding process, as with a slide rule, to convert the vertical-incidence values to the required

oblique incidence values. Suppose that we have an experimental $P'f$ curve, and that we assume that it corresponds to a layer whose lower edge is at a height H above the surface of the earth. (Since $P' = 2h'$, whereas in practice h' is plotted against f , it will be better from now on to refer to $h'f$ curves.) For a given point (h', f) we work out the value of $\tan \alpha$ for a given distance y as above. α does not depend on f but only on h' , and so a graph of h' as ordinates and $\sin \alpha$ as abscissae can be constructed. Such a graph with $\sin \alpha$ on a logarithmic scale is called a transmission curve.

If now the $h'f$ curve is plotted with f on a logarithmic scale as abscissa, and the transmission curve is slid over it until the two coincide at the height h' , the ordinate corresponding to $\sin \alpha = 1$ will lie on the ordinate corresponding to a frequency

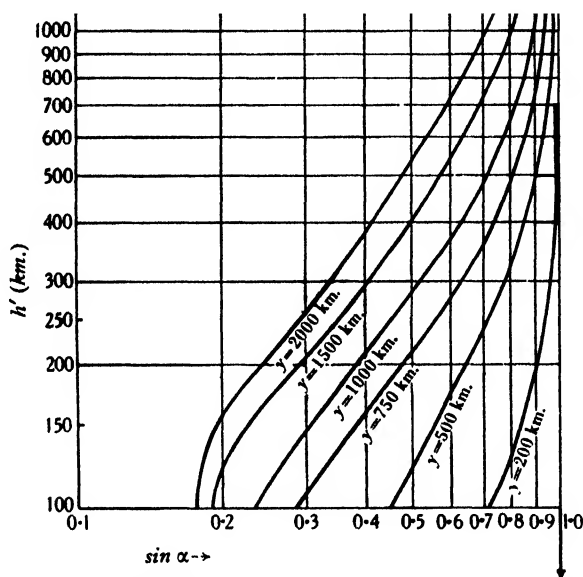


Figure 4. Transmission curves for various distances from the transmitter.

$f \operatorname{cosec} \alpha$, which from equation (3.6) is equal to f_{ob} . We can thus read off directly the equivalent frequency f_{ob} corresponding to any point on the $h'f$ curve. As the transmission curve is moved from right to left, it initially touches the $h'f$ curve, and the corresponding value of f_{ob} represents the skip frequency. For values of f_{ob} between the skip frequency and the critical frequency at vertical incidence, the transmission curve will cut the $h'f$ curve in two places corresponding to the low-angle and high-angle pair of rays which, as is well known, are obtained at oblique incidence under these conditions. From the abscissa scale of $\sin \alpha$ on the transmission curves the value of $\sin \alpha$ can be read off directly, for any point at which the transmission curve cuts the $h'f$ curve, for insertion into equation (2.15) to relate the absorption at oblique incidence with that measured at vertical incidence.

For short distances the transmission curves depend very little on the choice of H within the practical range, because the value of k is always very near to unity. For values of y over 1000 km. the curves differ appreciably for different values of H ,

but run together for large values of h' . For extreme distances for which $y > \sqrt{8r_0 H}$, i.e. $l > 1$, we must remember that the transmission curve can only be drawn for values of h' greater than $(2l-1)H$. This may mean under certain conditions that transmission by a single hop to these distances is only possible by the high-angle ray.

In practice it would be inconvenient to have to use a separate transmission curve for each assumed value of H , and a composite curve can be made which will be accurate enough, and within the limits to which we are justified in working. We assume that from $h' = 100$ km. to $h' = 150$ km. we may take H equal to 100 km., and that from $h' = 200$ km. to $h' = 250$ km. we may take H equal to 200 km. while for all values of h' above 300 km. we may take H equal to 300 km. We then draw a composite curve joining these three sections, and figure 4 shows a set of such curves drawn for various values of the distance y . In these curves h' has also been plotted on a logarithmic scale to reduce the steepness of the curves, and this is an advantage also in the corresponding $h'f$ curves in reducing the steepness in the region of the critical frequency.

Before discussing the practical application of these transmission curves, we will turn to the consideration of equivalent heights at oblique incidence.

§ 5. EQUIVALENT HEIGHT ANALYSIS AT OBLIQUE INCIDENCE

At vertical incidence, with the standard pulse technique with a cathode-ray indicator and a linear time base, the displacement of the echo beyond the ground-ray pulse gives a direct measurement of the time t taken by the pulse to travel up into the ionosphere and back, i.e. it gives a measure of P' (equal to ct) and of h' (equal to $P'/2$). But at oblique incidence, if we assume the ground-ray pulse to be still present, the displacement of the echo corresponds to the difference between the equivalent path P'_{ob} and the distance y over the ground. If therefore we define the equivalent height h'_{ob} in terms of the displacement of the echo from the ground ray, we have*

$$h'_{ob} = \frac{1}{2} (P'_{ob} - y).$$

Even when we are beyond the range of the ground ray it is convenient to keep to this definition rather than to use $h'_{ob} = \frac{1}{2} P'_{ob}$, since, although changes of h'_{ob} with P'_{ob} will be the same on either definition for a given value of y , at extreme distances while P'_{ob} gets very large, $(P'_{ob} - y)$ tends to smaller values. If a transmitter being used for a $P'f$ run at vertical incidence were observed on a receiver at the distance y , the variation in the position of the reflected pulse would give a measure of the variation of h'_{ob} with frequency. Corresponding to the $h'f$ curve obtained at vertical incidence there is an $\{h'_{ob}, f_{ob}\}$ curve at oblique incidence, which we refer to the position of the ground ray as datum.

Except at extreme distances, we can obtain a relation between h'_{ob} and h' in

* It is important to notice that equivalent height as here defined is different from the height of the equivalent triangular path in the flat-earth case. It is the equivalent height to which the echo displacement at oblique incidence would correspond if it were obtained at vertical incidence.

a simple way. We consider first the difference between P_1' and y_1 in figure 2. From the triangle TOT' we have immediately

$$P_1' = r_0 \sec \alpha \sin \phi_1 = y_1 \sec \alpha \frac{\sin \phi_1}{\phi_1} \quad \dots\dots(5.1),$$

so that when ϕ_1 is small

$$P_1' - y_1 = y_1 (\sec \alpha - 1) \quad \dots\dots(5.2).$$

Also assuming that the ratio of P_2' in the layer to y_2' is large compared with the ratio of y_2' to y_2 , i.e. neglecting a factor $(1 + H/r_0)$, we have

$$P_2' = y_2 \sec \alpha$$

$$\text{and} \quad P_2' - y_2 = y_2 (\sec \alpha - 1) \quad \dots\dots(5.3).$$

Combining equations (5.2) and (5.3), and allowing for the two P_1' portions in the path P'_{ob} , we get

$$P'_{ob} - y = y (\sec \alpha - 1) \quad \dots\dots(5.4).$$

With the formula for $\tan \alpha$ in equation (3.9), and the relation $P' = 2h'$, equation (5.4) leads to

$$h'_{ob} = h' k \tan^2 \alpha \quad \dots\dots(5.5).$$

This is the flat-earth case modified by the factor k . At the extreme distances, where the angles of elevation concerned may be small, we can no longer ignore the terms of the order of H/r_0 omitted above. Returning to equation (5.1), we write

$$\begin{aligned} 2P_1' &= 2y_1 \sec \alpha (1 - \phi_1^2/6) \\ &= 2y_1 \sec \alpha - \frac{1}{3} (y_1^3/r_0^2) \sec \alpha \quad \dots\dots(5.6). \end{aligned}$$

Substituting for y from equation (3.12), we have

$$\frac{1}{3} \frac{y_1^3}{r_0^2} \sec \alpha = \frac{\sec \alpha}{3 r_0^2} \frac{1}{8} \left(\frac{km - m + 1}{km} \right)^3 y^3.$$

We now substitute for y^2 from equation (3.13), and for y from equation (3.9), and find that

$$\frac{1}{3} \frac{y_1^3}{r_0^2} \sec \alpha = \frac{1}{3} P' \frac{H}{r_0} (k-1) (km - m + 1) \operatorname{cosec} \alpha \quad \dots\dots(5.7).$$

For P_2' we must now use the form in equation (3.5), i.e.

$$P_2' = (P' - 2H) \operatorname{cosec} \alpha,$$

and from equation (3.4)

$$\operatorname{cosec} \alpha' = \operatorname{cosec} \alpha \left[1 + \frac{H}{r_0} \cos^2 \alpha \right].$$

Thus $P_2' = (P' - 2H) \operatorname{cosec} \alpha + (P' - 2H) \frac{H}{r_0} \cos^2 \alpha \cdot \operatorname{cosec} \alpha,$

and using equations (3.7) and (3.10) this becomes

$$P_2' = y_2 \sec \alpha + P' \left(1 - \frac{1}{m} \right) \frac{H}{r_0} \cos^2 \alpha \operatorname{cosec} \alpha \quad \dots\dots(5.8).$$

Combining equations (5.6), (5.7) and (5.8), we have

$$h'_{ob} = h' \left(k \tan \frac{\alpha}{2} + A \frac{H}{r_0} \operatorname{cosec} \alpha \right) \quad \dots\dots(5.9),$$

where

$$A = \left(1 - \frac{1}{m} \right) \cos^2 \alpha - \frac{1}{2} (k - 1) (km - m + 1) \quad \dots\dots(5.10).$$

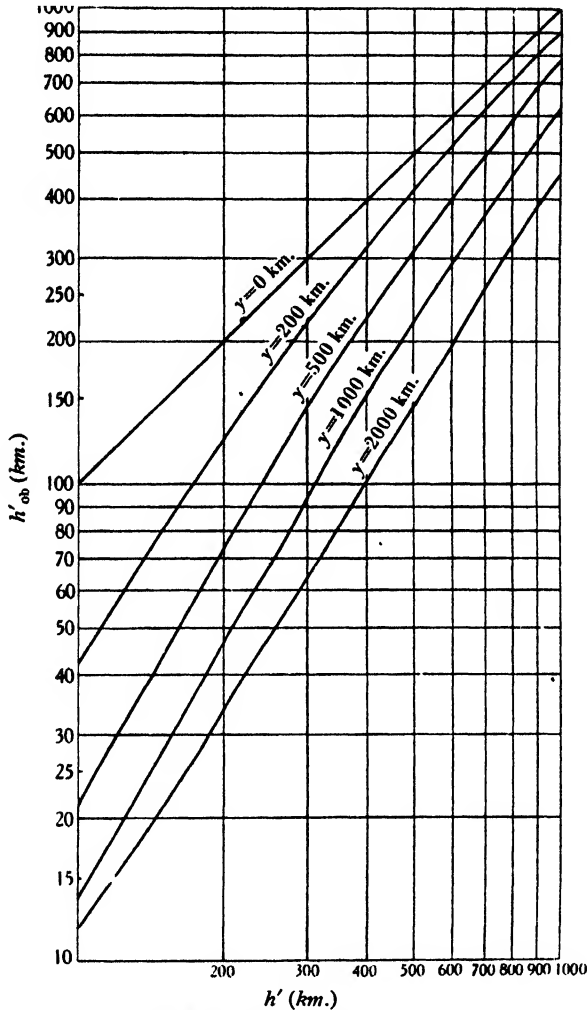


Figure 5. The equivalent height h'_{ob} as a function of h' for various distances from the transmitter.

We notice that although $\operatorname{cosec} \alpha = 1$ at vertical incidence when $\alpha = 90^\circ$, A is zero since $k = 1$ and $\cos \alpha = 0$, whatever the depth of penetration into the layer determined by m . The value of h'_{ob} therefore reduces to h' as it should. For small angles of elevation at extreme distances the correction term becomes comparable with the term $k \tan \frac{\alpha}{2}$. As a check if we consider the ray leaving the earth tangentially

and with mirror reflection, for which $k=2$, $m=1$, $\alpha = \sqrt{(2H/r_0)}$, so that $A = -\frac{2}{3}$ and $h' = H$. Then

$$k \tan \frac{\alpha}{2} = \sqrt{\frac{2H}{r_0}}$$

and

$$\frac{H}{r_0} \operatorname{cosec} \alpha = \sqrt{\frac{H}{2r_0}},$$

$$h'_{ob} = H \left[\sqrt{\frac{2H}{r_0}} - \frac{2}{3} \sqrt{\frac{H}{2r_0}} \right] = \frac{2}{3} H \sqrt{\frac{2H}{r_0}}.$$

But in this simple case

$$h'_{ob} = r_0 [\tan \phi_1 - \phi_1] = \frac{1}{3} r_0 \alpha^3,$$

since $\phi_1 = \alpha$ for the tangent ray. Thus

$$h'_{ob} = \frac{1}{3} r_0 \left(\frac{2H}{r_0} \right)^{\frac{3}{2}} = \frac{2}{3} H \sqrt{\frac{2H}{r_0}} \text{ as above.}$$

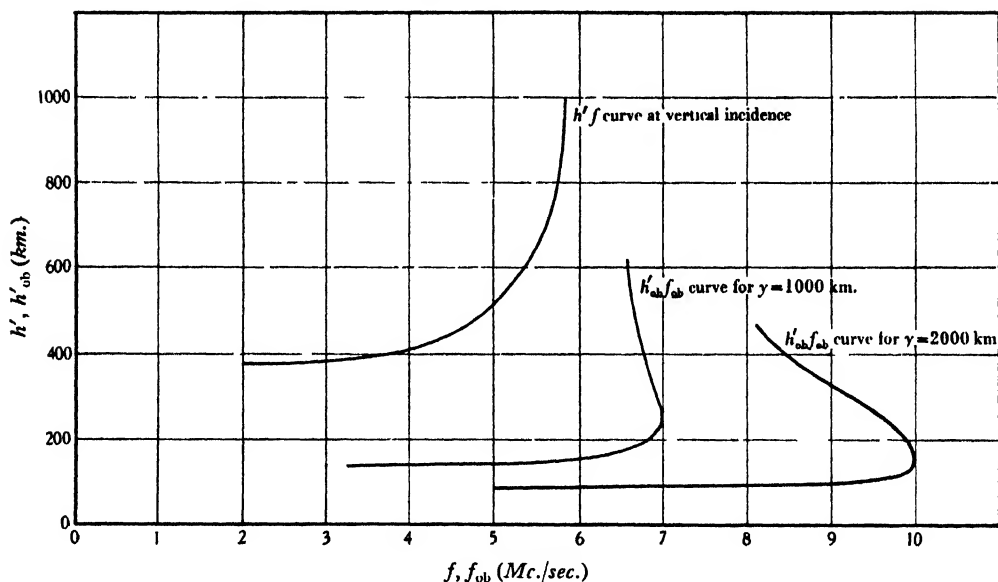


Figure 6. $h'_{ob} f_{ob}$ curves for $y=1000$ km. and $y=2000$ km., for a given $h'f$ curve at vertical incidence.

We have seen that for a given H and y the angle α is a function of h' only, so that it follows from equation (5.9) that h'_{ob} is a function of h' only. We can, therefore, draw a curve of h'_{ob} against h' for a set of values of H and y . Figure 5 shows such a set for various values of y , where the curves are again made composite to compromise for the variation with H . These curves have also been drawn on logarithmic scales. By using these curves in conjunction with the transmission curves in figure 4, the $h'_{ob} f_{ob}$ curve for any distance y corresponding to a given $h'f$ curve at vertical incidence can be quickly drawn out. Figure 6 shows a typical $h'f$ curve drawn on an ordinary linear scale. This is redrawn with h' and f on

logarithmic scales, and for any point $h'f$ the value of f_{ob} for the chosen distance y is obtained by using the appropriate transmission curve. The value of h' is then used to find h'_{ob} from the appropriate curve in figure 5. It is quite a quick process to tabulate h'_{ob} , f_{ob} for a series of points on the $h'f$ curve, and the result of so doing for $y=1000$ km. and 2000 km. is shown in figure 6. We can see from this figure the advantage of defining h'_{ob} as $\frac{1}{2}(P'_{ob}-y)$ rather than as $\frac{1}{2}P'_{ob}$, since it allows us to draw the $\{h'_{ob}, f_{ob}\}$ curves conveniently on the same axes as the $h'f$ curve.

§ 6. THE CONSTRUCTION OF {RANGE, ANGLE-OF-ELEVATION} CURVES

We can see at once from the shape of the $\{h'_{ob}, f_{ob}\}$ curves the relative positions of the low-angle and high-angle rays on any frequency above the critical frequency at vertical incidence, up to the skip frequency where the two rays coalesce. It would be useful, however, to be able to predict the results which would be obtained at any given frequency at oblique incidence, without having to work out the whole of the $h'_{ob}f_{ob}$ curve. This we can do by using the transmission curves, in conjunction with the vertical-incidence $h'f$ curve, to work from the assumed value of f_{ob} to the equivalent points on the $h'f$ curve.

The ordinate corresponding to $\sin \alpha = 1$ on the transmission curves is set over the ordinate corresponding to the chosen f_{ob} , and then the intersection of the transmission curve for the assumed distance y with the $h'f$ curve gives the values of h' (in the general case when both the low-angle and high-angle rays are present), from which the values of h'_{ob} can be obtained by using the appropriate curve in figure 5. From the values of f_{ob} and the equivalent values of f we can calculate $\sin \alpha$, and obtain the angles of elevation α at which the rays enter the layer. At short distances the angle α will be effectively the same as the angle of elevation α_0 at the ground, but at extreme distances the true relation between α_0 and α must be used; from equation (2.2) this is

$$\cos \alpha_0 = \left(1 + \frac{H}{r_0}\right) \cos \alpha.$$

But, as we have seen in deriving the transmission curves, the angle α for a given distance y and equivalent height h' is only a function of h' , so that it is possible to plot out a series of curves for α_0 against h' analogous to the $\{h', h'_{ob}\}$ curves in figure 5. For the extreme distances the angle of elevation will depend considerably upon the value of H chosen, but up to about $y=2000$ km. we can draw a single set of curves, as in the case of h'_{ob} , and such a set is given in figure 7.

From these curves it is possible to construct a set of curves showing the distance y to which a ray travels, as a function of the initial angle of elevation α_0 for a series of frequencies, assuming, of course, the form of the $h'f$ curve at vertical incidence. The curves in figure 8 were actually worked out from an assumed sine-squared law of gradient in the layer, in which H is taken as 200 km. and the maximum density occurs 300 km. above the ground. They are taken from a paper by T. L.

Eckersley⁽³⁾, which should be consulted for details of the method of computation. These curves show in another way that for a given range or distance there are two possible rays for each frequency between the penetration frequency at vertical incidence and the skip frequency corresponding to the nose of the $h'_{\text{ob}} f_{\text{ob}}$ curve.

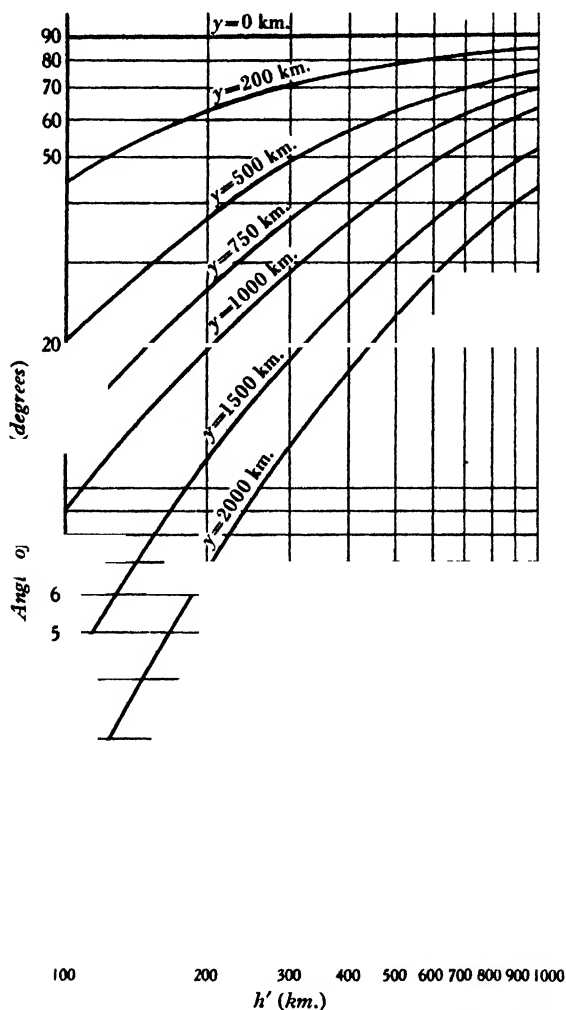


Figure 7. Angle of elevation as a function of h' for various distances from the transmitter.

They also show clearly why the skip frequency appropriate to a given distance is the maximum frequency receivable at that distance, since although the layer can return higher frequencies to the earth, they will for all angles of elevation be transmitted over the point in question, and come to earth again at some point beyond. For each frequency above the penetration frequency at vertical incidence there is a critical angle at which the ray escapes, and this angle is in general only slightly greater than the skip angle corresponding to the minimum range or skip distance.

The energy contained between these two angles at the transmitter is thus spread out on return to the earth from the skip distance to all greater distances; Eckersley's paper⁽³⁾ may be consulted for a more detailed discussion of this point. This effect, coupled with the high absorption due to long traverse in the denser parts of the

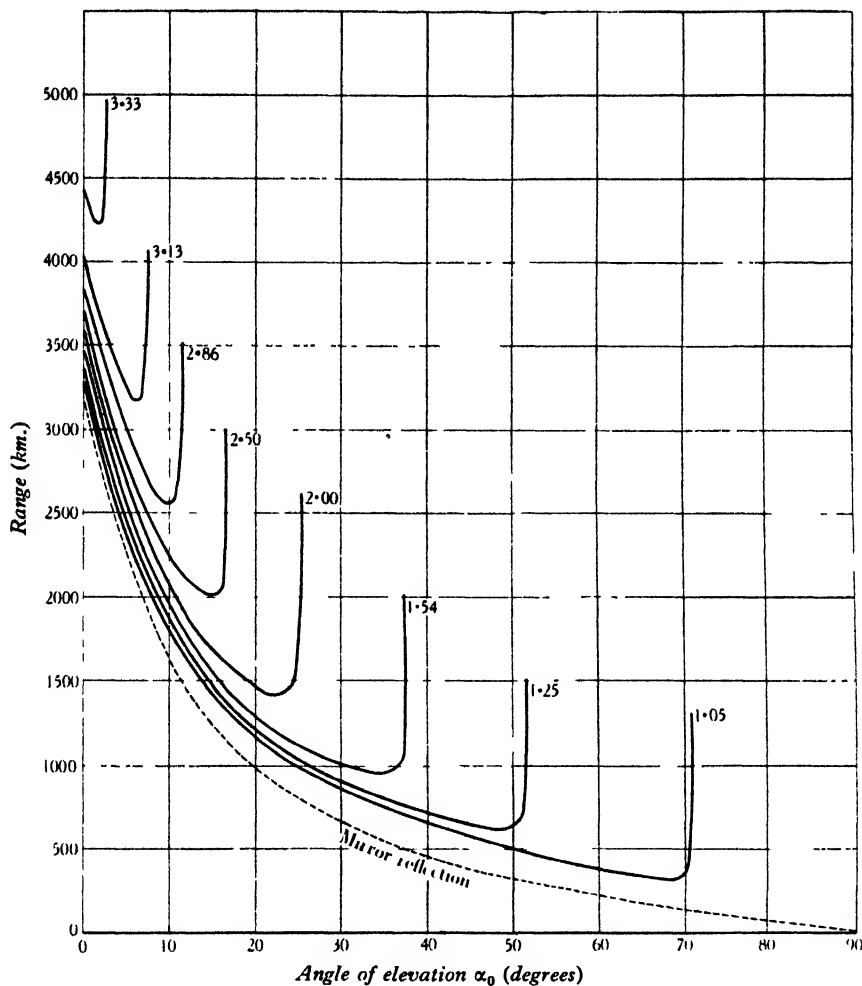


Figure 8. Range curves as a function of the angle of elevation for various values of f_{ob}/f_0 .

layer, explains why in practice the upper limb of the $h'_{ob}f_{ob}$ curve is extremely weak, and why it can only be observed in the region of the skip frequency.

The $h'_{ob}f_{ob}$ curve at any distance can be associated with the set of curves in figure 8 by considering the section of the curves made by the appropriate abscissa. We can see at once the important point that the nose of the $h'_{ob}f_{ob}$ curve does not correspond to the penetration frequency at vertical incidence, but that as derived from Martyn's theorem it corresponds to a point some way down the $h'f$ curve at

vertical incidence. The part of the curve above this point becomes on application of the theorem (i.e. by the use of the transmission-curve technique) the upper or high-angle limb of the $h'_{ob}f_{ob}$ curve.

§7. THE CONSTRUCTION OF {SKIP-FREQUENCY, DISTANCE} CURVES

It is obvious from a practical point of view that the skip frequency at a given distance is a very important factor in oblique transmission problems, since it represents the maximum possible receivable frequency at that distance. It is therefore useful, in connexion with any given $h'f$ curve, to plot out with the aid of the transmission curves a curve of skip frequency as a function of distance from the transmitter. In interpreting this curve it is useful to bear in mind the complementary picture of figure 8, since it shows clearly how, as the range increases, the skip frequency increases, and approaches at extreme distances to the maximum escape frequency corresponding to the penetration of the ray which leaves the earth tangentially. Returning to equations (2.9) and (2.10), in which we may consider

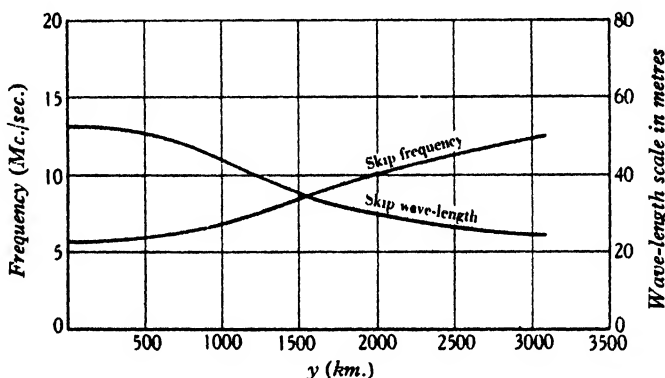


Figure 9. Skip frequency and skip wave-length as a function of the distance from the transmitter, derived from the $h'f$ curve in figure 6.

the layer to reach to the surface of the earth as far as the analysis is concerned, we replace h_0 by $(H + h_{\max})$, where as before H is the actual height of the lower edge of the layer, and h_{\max} is the height above this lower edge at which the maximum density occurs. If we then write f_0 as the critical penetration or escape frequency at vertical incidence, the escape frequency f_{ob} for a ray leaving the earth with an angle of elevation α_0 is given by

$$f_{ob} = f_0 / \sqrt{\sin^2 \alpha_0 + \frac{2(H + h_{\max})}{r_0} \cos^2 \alpha}$$

For large angles of elevation this reduces to the flat-earth case of $f_0/\sin \alpha_0$, but for the tangent ray $\alpha_0 = 0$, and the maximum escape frequency is $f_0 \sqrt{r_0/2(H + h_{\max})}$.

Figure 9 shows a {skip-frequency, distance} curve deduced from the $h'f$ curve given in figure 6; the corresponding {skip-wave-length, distance} curve is also shown, since it is often useful for the engineer to think in terms of wave-length

rather than of frequency. It will be seen that as the distance increases, the skip frequency approaches an upper limit, and in identifying it with the maximum escape frequency as above, we have to assign a value to $(H + h_{\max})$, i.e. the actual height above the ground at which the maximum density occurs. If we assume that h_{\max} is small compared with H , we can take as an approximate value the value of h' corresponding to the lower limit of the $h'f$ curve under consideration (in the present case 380 km.). It is therefore useful to have a curve of $\sqrt{(r_0/2H)}$ as a function of H , given in figure 10, as a factor for obtaining the limiting frequency at extreme distances, from the penetration frequency at vertical incidence.

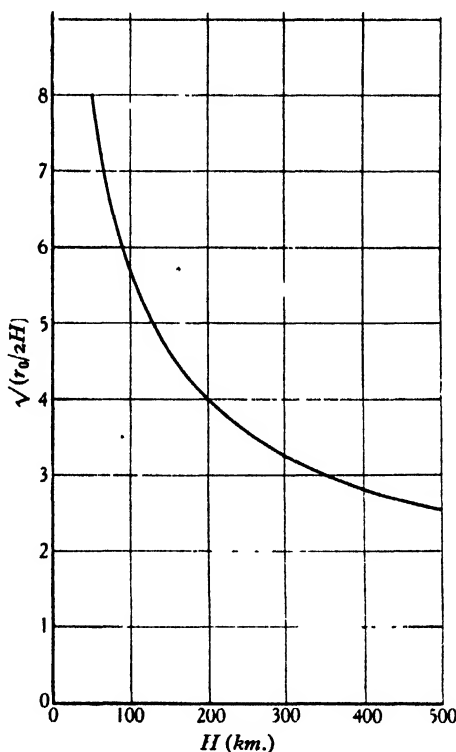


Figure 10. $\sqrt{(r_0/2H)}$ as a function of H , to give the limiting value of f_{ob}/f_0 at extreme distances.

We have to bear in mind here a point which has already been raised—that when the lower edge of the layer is at a height H , rays can only reach distances greater than $\sqrt{(8r_0H)}$ by a single hop when the equivalent frequency at vertical incidence penetrates to an equivalent height of at least $(2l - 1)H$, l being the parameter given by equation (3.14). At these longer distances, say those greater than 2000 km., the shape of the transmission curves becomes increasingly dependent on the value of H assumed, and as far as the simple geometrical picture of the ray-path is concerned, the detailed analysis given above gives a clearer idea of what is happening than the simplified picture given by Smith; his picture is equivalent to assuming

that at oblique incidence there is mirror reflection at a height h' , the corresponding equivalent height at vertical incidence.* If we put $m = 1$ in equation (3.13) so that

$$k = \frac{y^2}{8r_0 H} + 1,$$

and if we substitute in equation (3.9), remembering that P' is here $2h'$, and that H is h' , we get

$$\tan \alpha = \frac{2h'}{y} + \frac{y}{4r_0}.$$

Smith uses $\cot \phi_0$ instead of our $\tan \alpha$, and gives

$$\cot \phi_0 = \frac{h' + r_0(1 - \cos \theta)}{r_0 \sin \theta}, \quad \text{where } \theta = y/2r_0,$$

which gives $\frac{2h'}{y} + \frac{y}{4r_0}$ when θ is small.

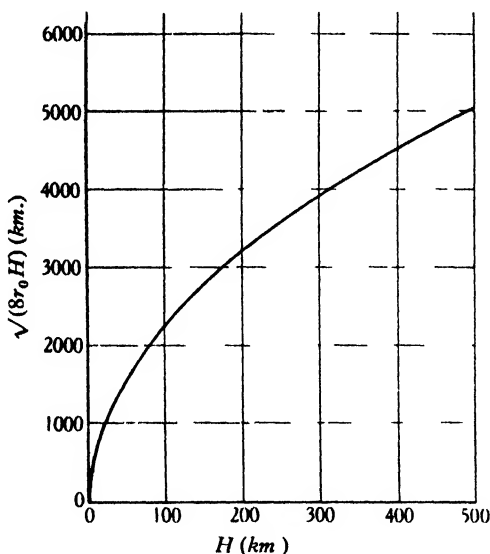


Figure 11. $\sqrt{(8r_0 H)}$ as a function of H to give the limiting distance of a single-hop transmission.

If we draw a transmission curve for one of these longer distances, we have to terminate it at its lower end at $h' = (2l - 1)H$, and it will be seen that as the distance considered is increased beyond $\sqrt{(8r_0 H)}$, a point is reached at which the truncated transmission curve will only cut the $h'f$ curve once for values of f_{ob} greater than f_0 . This implies that at these distances single-hop transmission is only possible with a high-angle ray. In practice, therefore, we should not expect to get a workable signal by a single hop much beyond the distance $\sqrt{(8r_0 H)}$. It is therefore useful to have a curve of $\sqrt{(8r_0 H)}$ as a function of H , and this is given in figure 11.

The analysis can be applied to the case of multiple hops by considering, in the case of n hops, the distance y/n for the determination of f_{ob} . The equivalent h'_{ob}

* While this paper has been in the press, N. Smith⁽⁴⁾ has published another paper in which he gives a further correction for the curvature of the earth.

will be n times the value of h'_{ob} so obtained. In this way we can study the formation of multiple-echo patterns, and see how at long distances the first echo received may correspond to $n=3, 4$ or even more, where smaller values of n only are possible for the heavily attenuated high-angle ray. In this connexion it is again interesting to refer to the discussion on multiple echoes given on pp. 410 to 412 of Eckersley's paper⁽³⁾.

§ 8. THE EFFECT OF A HORIZONTAL GRADIENT OF ELECTRONIC DENSITY AND OF THE EARTH'S MAGNETIC FIELD

As was pointed out in the introduction, the above analysis has been worked out on the assumption that there is no horizontal gradient of electronic density and no magnetic field. We have seen that starting from these premises the analysis can be developed to take account of the earth's curvature even at long distances, but we must now consider to what extent our results are modified by the inclusion of these two factors.

The presence of a horizontal density-gradient will in general cause a ray to emerge at a different angle of elevation from that at which it entered the layer, and unless the transmission is along a contour of equal maximum electronic density or at right-angles to the contours, the ray will suffer a lateral deviation. By assuming some law for the horizontal gradient it is possible to study these effects analytically, but it is clear that they both modify the simple picture we have analysed. The error will be greatest for a transmission at very oblique incidence across the density contours, in which the ray remains for long distances in the layer.

If we consider a single hop in which the incidence is not too oblique, so that the ray is actually only in the layer for a comparatively short distance, we can assume that there is no horizontal gradient over this region. We can then refer the process to the density conditions at the apex of the path, i.e. mid-way between the transmitter and the receiver. This implies that the vertical $h'f$ measurements should be made at this mid point. In testing out the theory over a given distance it is not necessarily feasible to make vertical-incidence measurements at the mid point, but as a compromise it may be possible, by making measurements at both ends of the path and averaging them, to get an idea of the characteristics at the mid point.

The effect due to the earth's magnetic field is very difficult to assess owing to the complexity of the magneto-ionic theory. In this theory the magnetic field enters through the term τ , which is the ratio of the gyromagnetic frequency f_H to the transmitted frequency. As is well known, at vertical incidence the extraordinary escape frequency exceeds the ordinary escape frequency by $f_H/2$ when τ is small. Now if we assume that at vertical incidence the $h'f$ curve for the extraordinary ray when plotted logarithmically is of the same shape as the curve for the ordinary ray, but shifted to the right, as in figure 12, so that the extraordinary escape frequency is greater by $f_H/2$ than the ordinary escape frequency, and if we then apply the transmission-curve technique to each, the $h'_{ob}f_{ob}$ curves obtained will be similar in shape and have the same shift, owing to the use of a logarithmic scale. The

noses P and Q of the curves will correspond to two similar points O and E on the $h'f$ curves, and their actual separation in frequency will be $\frac{1}{2}f_H \operatorname{cosec} \alpha$, where α is the angle of elevation appropriate to the equivalent height h' for the particular distance we are considering. (We are assuming that the frequencies at O and E are sufficiently near to their respective escape frequencies for their difference to be considered as $\frac{1}{2}f_H$.) The appropriate value of $\operatorname{cosec} \alpha$ is simply given by the ratio of f_{ob}/f , the frequencies at P and O .

Referring again to the curves in figure 8, we see that the skip frequency for a given distance escapes through the layer for an angle which is only slightly greater than the skip angle, so that we may for the purposes of the present argument identify

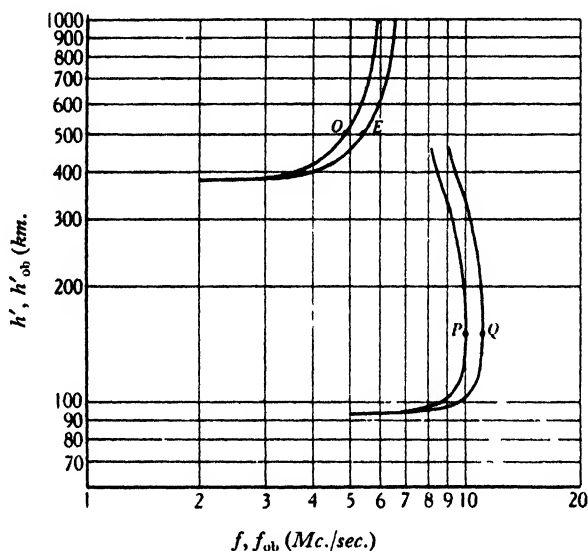


Figure 12. h'_{ob}, f_{ob} curves for ordinary and extraordinary rays derived from the equivalent $h'f$ curves, assuming that the equivalence theorem can be applied.

approximately the skip frequency with the frequency of the ray which just escapes when transmitted at the skip angle. Now by assuming an oblique transmission with a vertical magnetic field, it can be seen that if we consider the value of the difference of the escape frequencies ($f_{ext} - f_{ord}$) as a function of the angle of elevation α , then, provided τ is less than about 0.7, the value decreases below the value at vertical incidence as α decreases from 90° , and reaches a flat minimum before increasing up to infinity as α approaches zero. Moreover, this minimum occurs when $\alpha \approx 36^\circ$ independently of the actual value of τ , and*

$$(f_{ext} - f_{ord})_{oblique} \approx \frac{2.6\tau}{1 + \tau} (f_{ext} - f_{ord})_{vertical}.$$

Thus instead of a factor of $\operatorname{cosec} \alpha$ (which = 1.7 when $\alpha = 36^\circ$), we have a factor which is less than unity.

* I am indebted to Mr T. L. Eckersley for some analysis from which these results have been deduced.

From these results it seems safe to deduce that for most practical cases the value of $(f_{\text{ext}} - f_{\text{ord}})$ at the noses of the $h'_{\text{ob}}f_{\text{ob}}$ curves decreases as the distance from the transmitter increases, instead of increasing as the simple application of the theorem would suggest. Actually the shape of the $h'_{\text{ob}}f_{\text{ob}}$ curve cannot strictly be obtained from the vertical-incidence $h'f$ curve by means of the transmission curves, but it is reasonable to suppose that the process will be nearly true for the ordinary ray. If then for the vertical-incidence $h'f$ curve for the ordinary ray we construct the {skip-frequency, distance} curve as for figure 9, and take this to be correct for the ordinary ray, we know that the corresponding extraordinary curve will start with a separation of $\frac{1}{2}f_H$, and will then gradually close in towards the ordinary curve as the distance is increased.

Some idea of the way in which the two curves will converge can be obtained from the relation in terms of τ given above. This would seem to be a better way of allowing for the effect of the magnetic field than, say, applying the transmission curve technique to a curve sketched in between the vertical incidence $h'f$ curves for the ordinary and extraordinary rays.

§9. PRACTICAL APPLICATION OF THE ANALYSIS

The analysis we have been considering has its most practical application in the prediction of the behaviour of short waves over long distances, for determining the choice of frequencies to be used over any given route. Such routes can be divided into two classes according as they are of medium distance, where single-hop transmission is possible, or of extreme distance where the transmission is only possible by multiple hops. The latter case may be taken first, and as regards the optimum frequency to be used, we can restrict ourselves to the consideration of the case where the individual hops themselves represent long distances and low angles of elevation, since steeper angles imply lower usable frequencies and more overall attenuation.

In an idealized case the problem may be treated as a succession of similar hops, each one of which can be treated as for a single-hop transmission. In practice, however, owing to the changing density conditions en route, the path of any given order of echo will consist of a series of unequal hops, and the angle at which the ray enters and leaves the layer may change along the route. Moreover the signal which is received at an extreme distance will in general be the resultant of several low-angle rays, and the assessment of the total absorption under these conditions will be a complex problem. Actually the overall absorption is found to be equivalent to a transmission through a succession of grades of ionic density, so that the attenuation can be represented by $e^{\sum (-k_1 d_1)}$. Theoretically the coefficients k should be deducible by applying the absorption theorem to vertical-incidence measurements for a set of low-angle rays. In practice, however, they are obtained by analysing a large mass of practical long-distance transmission data. In determining the practicability of a given route, we have to consider the two major factors of electron limitation and absorption, and to remember that to some extent they represent opposing conditions.

We cannot go further here into this aspect of the problem, but it is obvious that in analysing any given route it would be most useful to know the density-distribution at every point along the route, so that it might be possible to deduce the absorption and the limiting frequency for low-angle rays for the different parts of the route. This serves to emphasize the need for regular vertical-incidence measurements at a large number of places in different parts of the world, so that the probable density-distributions at any place at any time and season may be predicted.

Coming now to the consideration of single-hop transmissions, and applying the transmission-curve technique, we have in practice to take account of the fact that the $h'f$ curve is not usually a curve of the simple type given, for instance, in figure 6, but results from the combined effects of the E and F layers. It is easily seen that a lower layer, for which the vertical-incidence escape frequency is less than that for a higher layer, may nevertheless control the skip frequency when both layers are present together. Thus in summer when the F_1 layer is well defined, it may control the skip frequency beyond a certain distance from the transmitter, and at still greater distances the E layer may take charge, although the vertical escape frequency may be considerably less than for the F_2 layer. This latter effect is especially likely in summer, because the E maximum density is then greater than in winter, while the F_2 density is considerably less and the layer-height markedly greater than in winter, and it accounts for the fact that distant stations working on, say, 15 m. are sometimes out of the skip, when a casual measurement of the F_2 escape frequency would suggest that the limiting wave-length should be much longer.

In deducing, therefore, from the vertical $h'f$ curve the {skip-frequency, distance} curve of the type shown in figure 9, this possible shielding of the F layer by the E layer has to be taken into account, but provided that the set of transmission curves is applied to the complete $h'f$ curve, this is allowed for in the graphical process, which shows immediately the distance at which the lower layer takes charge.

For an assumed value of H we have seen that we should not expect to get a workable signal much beyond a distance $\sqrt{(8r_0H)}$ given in figure 11, and that at this distance the maximum transmissible frequency is approaching the maximum escape frequency $f_0\sqrt{(r_0/2H)}$, where f_0 is the vertical escape frequency. In practice these theoretical limits must be somewhat reduced. It is necessary to allow a small margin of safety in order not to work too near to the edge represented by the skip frequency. Further, the factor should be reduced to allow for the actual depth of penetration into the layer; and since a ray leaving the transmitter tangentially would be heavily absorbed by the ground before getting clear, it is usual to assume that the initial angle of elevation should be somewhat greater than zero, say about 5° , and the polar diagram of the aerial is usually adjusted accordingly. These considerations lead to the choice of an optimum frequency which is less than the skip frequency, and some corresponding arbitrary factor could be incorporated as a reduction factor in the curves of figures 10 and 11. But it is felt that it is better to give the ideal curves, and to indicate in general terms, as above, the necessary modifications. The method of allowing for the effect of the earth's magnetic field

has been given above to take account of the fact that the extraordinary ray, rather than the ordinary ray, determines the maximum usable frequency, whereas the vertical-incidence $h'f$ curve for the ordinary ray is used for deducing the oblique-incidence curve.

Mention has already been made of the importance in accurate work of knowing the density-distribution at the mid point of the path rather than at either end, especially for experiments designed to test out the fundamental soundness of the analysis. When a pulse transmission is received at a medium distance from the transmitter, the echo pattern obtained can be very complex as a result of possible multiple hops, low-angle and high-angle pairs, ordinary and extraordinary pairs due to magneto-ionic splitting, and simultaneous reflections from different layers. From a knowledge of the vertical-incidence $h'f$ curve, the positions of the various possible echoes for the given distance and frequency can be predicted, and this provides a check on the theory, and conversely aids in the interpretation of the complex echo pattern actually obtained.

By keeping a watch on the vertical-incidence conditions, the course of a $P't$ run on a fixed frequency at a given distance can be deduced. For instance, if a run is taken during the evening, when the general level of electronic density is falling, the appearance of the high-angle ray and its movement in towards the corresponding low-angle ray, with eventual coalescence as the signal goes into the skip, can be interpreted in a simple graphical way, by considering the gradual shift to the left of the $h'_{ob}f_{ob}$ curve, as the $h'f$ curve moves to the left with decreasing density.

§ 10. CONCLUSION

Although the analysis given in this paper admittedly refers to an ideal case, and the necessary modifications (in particular that due to the earth's magnetic field) can only be expressed in a rather qualitative way, it is found in practice to be very useful in the explanation of oblique-incidence transmission phenomena. Graphs such as figures 3, 4, 5, 7, 10 and 11, which can be applied to any given $h'f$ curve to give curves of the type shown in figures 6, 8 and 9, will, it is hoped, form a helpful tool in the hands of those who are engaged on oblique-incidence and long-distance transmission problems.

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THE NUCLEAR MAGNETIC MOMENT OF COPPER

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ABSTRACT. The doublet hyperfine structures of the resonance lines of the copper arc spectrum, $\lambda 3247$ and $\lambda 3274$, have been measured with a quartz Lummer plate. The lines are produced free from reversal effects, the doublet separations being respectively 379 and $405 \times 10^{-3} \text{ cm}^{-1}$. The following hyperfine structure interval factors are calculated: $3d^{10}4s^2S_{\frac{1}{2}} = 197.5$, $3d^{10}4p^2P_{\frac{1}{2}} = 14$ and $3d^{10}4p^2P_{\frac{3}{2}} = 4.8$ (all in $\text{cm}^{-1} \times 10^{-3}$). The mean nuclear magnetic moment for the two copper isotopes, 63 and 65, is derived from the ground state, $3d^{10}4s^2S_{\frac{1}{2}}$. The value found is $\mu = 2.47$ nuclear magnetons, this being probably a better estimate than that given by other terms, since the ground state is spherically symmetrical and thus not affected by quadrupole moment of the nucleus. By adopting Schüller and Schmidt's value for the ratio of the magnetic moments of the two isotopes, it is found that $\mu(^{63}\text{Cu}) = 2.43$ and $\mu(^{65}\text{Cu}) = 2.54$ nuclear magnetons.

§ 1. INTRODUCTION

THE nuclear spins of the two copper isotopes, 63 and 65, have been determined by Ritschl⁽¹⁾, who measured hyperfine structures in a number of the lines of the CuI spectrum. The spins of both the isotopes are the same, namely $\frac{3}{2}$. The spectrum was excited in a liquid-air-cooled hollow cathode, and amongst the lines measured were the two very intense resonance lines,

$$\lambda 3247 (3d^{10}4s^2S_{\frac{1}{2}} - 3d^{10}4p^2P_{\frac{1}{2}})$$

and

$$\lambda 3274 (3d^{10}4s^2S_{\frac{1}{2}} - 3d^{10}4p^2P_{\frac{3}{2}}).$$

From these the hyperfine structure splitting in the ground term $3d^{10}4s^2S_{\frac{1}{2}}$ can be derived, and as this in effect arises from a single s electron it is a term very well suited for the calculation of the nuclear magnetic moment. Fermi and Segré⁽²⁾, using Ritschl's data for this term, have evaluated a mean magnetic moment, assuming that the moments are nearly the same for both isotopes. They give $\mu = 2.42$ nuclear magnetons. Schüller⁽³⁾ has recalculated this from the same data, and after stating that Fermi and Segré have made a small numerical error, gives $\mu = 2.74$. This is no doubt a misprint, since in a later paper Schüller and Schmidt⁽⁴⁾ quote $\mu = 2.44$ as the value given by Ritschl's measurements upon the ground term.

Schüller and Schmidt⁽⁴⁾ have repeated Ritschl's observations upon two lines, $\lambda 5700 (3d^94s^2^2D_{\frac{3}{2}} - 3d^{10}4p^2P_{\frac{1}{2}})$ and $\lambda 5782 (3d^94s^2^2D_{\frac{5}{2}} - 3d^{10}4p^2P_{\frac{3}{2}})$, which, it will be noted, include as upper terms the upper levels of the two resonance lines. These investigators showed that the interval rule is not obeyed in the $3d^94s^2^2D_{\frac{3}{2}}$ term, and from it they derived both nuclear quadrupole moments and nuclear magnetic

moments. The latter were found to be different for the two isotopes, the calculated values being $\mu(^{63}\text{Cu}) = 2.52$ and $\mu(^{65}\text{Cu}) = 2.64$, and the weighted mean μ for both isotopes $= 2.56$. The value given for the quadrupole moment q is

$$-0.1 \pm 0.1 \times 10^{-24} \text{ cm}^2$$

The calculation of these quantities presupposes that the observed irregularities in the intervals are entirely to be attributed to a nuclear deviation from spherical symmetry, and it is clear from the high probable error given for q that uncertainties due to incomplete resolution will introduce small errors into the calculation of μ .

If there is a real quadrupole moment, the value of μ derived from the ground term is to be preferred since, being an S term, it is spherically symmetrical and therefore unaffected by any nuclear deviations from symmetry. It is thus clear that accurate measurements of hyperfine structure for the ground term are desirable. However, a difficulty exists here because the resonance lines are extremely sensitive to self-reversal. Early measurements by Back⁽⁵⁾ were vitiated by the existence of complete self-reversal. Frisch⁽⁶⁾ and Green and Wulff⁽⁷⁾ examined these lines with concave gratings but, consequently, the order of accuracy was not high. Sibaiya⁽⁸⁾ has attempted to measure the separations of the components by allowing complete self-reversal to take place, measuring to the centre of the reversal. The separation he reports for one line is in close agreement with that given here, but in the other line there is a deviation by 4 per cent.

Ritschl⁽¹⁾, who, owing to the use of a superior source, has no doubt succeeded in measuring these lines more accurately than the other observers quoted, discusses the question of self-reversal. The hollow cathode employed by him had an 8-mm. bore and was 10 cm. long. The result was that even with currents of only 50 ma. the resonance lines were completely reversed. He was obliged to use a current of 30 ma., with consequent long exposure, before he could eliminate reversal. He points out that, in spite of this, the lines were broadened, and he considers that his accuracy of measurement was not very high. That there still existed a certain amount of reversal is shown by the fact that the intensity ratio of the doublets seen by him was 2 : 1 instead of the theoretical ratio 5 : 3. The instruments used by Ritschl for measuring the structures were a reflection echelon and a Fabry-Perot interferometer coated with Hochheim alloy.

In the present paper are given details of measurements made upon the copper resonance lines, which have been obtained entirely free from reversal effects.

§ 2. EXPERIMENTAL DETAILS

The copper resonance lines $\lambda 3247$ and $\lambda 3274$ were obtained by accident in a water-cooled hollow-cathode tube which was being used to examine hyperfine structures in the spectra of iodine. The tube was a modified Schüller tube, the upper part of the cathode being a brass tube about 8 cm. in diameter and 18 cm. long, the lower hollow cathode portion having a bore of 1 cm. and a length of 15 cm. The lower portion was made of oxidized iron and was lined with platinum. Helium containing iodine vapour was continuously circulated through the tube at a pressure

of 2 mm. Under these conditions the narrow hollow cathode was filled with light and a rich iodine spectrum was emitted. When the helium pressure was reduced, a sudden change in the nature of the discharge took place at a critical pressure. The discharge left the narrow hollow cathode and filled the wide upper portion of the cathode cylinder. A peculiar change in the iodine emission spectrum was noticed. This will be discussed elsewhere. At the same time the copper resonance lines appeared in the discharge, and it is clear that they originated in the copper in the brass tube constituting the upper, and normally unused, portion of the discharge tube.

Even with currents reaching up to 500 ma., no trace of any other copper lines could be found, from which it is clear that the concentration of copper in the discharge must have been exceedingly minute. It is possible that the iodine attacked the brass wall and formed copper iodide, which would break up under bombardment and thus liberate free copper atoms into the discharge. Under all conditions

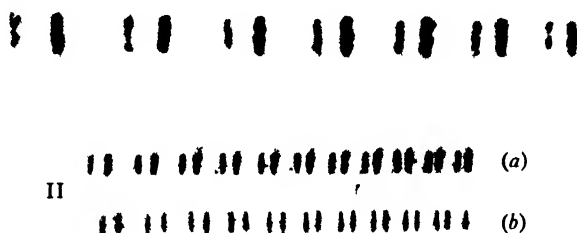


Figure 1. I, structure in $\lambda 3247$ ($\times 10$); II (a), structure in $\lambda 3247$ ($\times 4$); II (b), structure in $\lambda 3274$ ($\times 4$).

of excitation, and even with currents up to 400 ma., the lines remained exceedingly sharp, the hyperfine-structure components showing no trace of reversal and exhibiting intensity-ratios of approximately the theoretical values. This is remarkable when it is remembered that currents of 30 ma. produced a certain amount of reversal in Ritschl's experiments. It is not quite clear whether the discharge in the brass tube is a hollow-cathode discharge, but if it is, then the current-density must be very low. Ritschl's current-density was about 60 ma./cm², whereas when we used 150 ma., our current density was 3 ma./cm², if the whole tube was acting as a hollow cathode. This may explain why the lines are so sharp. On the other hand, the excitation mechanism is probably quite different from that which obtains in the normal hollow cathode, since we obtain good exposures, through the interferometer, in fifteen minutes, whereas Ritschl pointed out that with his current-densities long exposures were required. Whether the iodine or the tube diameter is the cause, the fact remains that the individual hyperfine-structure components were very sharp and yet the lines were strong. The separations could be measured with an accuracy of the order of 0.25 per cent.

The structures in the lines were measured with a quartz Lummer plate and checked with the aid of a variable-gap quartz Fabry-Perot interferometer coated

with aluminium. The Lummer plate, recently acquired from Adam Hilger Ltd., is a particularly fine one and is free from ghosts. When extreme overexposure is used, single lines show a shading off to one side, but under normal working conditions the instrument is entirely ghost-free. It is made of crystalline quartz, the length being 20 cm. and the thickness 0.342 cm. The resolving-power is high when the extraordinary ray is used, particularly when the emergence angle is near grazing. It may be pointed out that even in the visible region, where high reflecting coefficients are available, the Lummer plate is superior to the Fabry-Perot interferometer when the structures are so large that only a small-gap Fabry-Perot interferometer can be used.

The Lummer plate was set up before the slit of a quartz spectrograph. The latter was made in the laboratory and has a collimator focal length of 30 cm. and a camera focal length of 100 cm. The interferometer fringes were projected with a quartz fluorite achromat of focal length 21 cm., so that the effective focal length used for photographing the fringes was 70 cm. Since the Lummer plate is thin, the dispersion is large. In spite of the magnification, the individual components were very sharp, figure 2.

Since we are able to measure separations to 1 part in 1000 with this Lummer plate, Dr Simeon, of Messrs Adam Hilger Ltd., has kindly recalculated the dispersions for us. He has given us dispersions to four figures over the range 6500 to 2000 Å.

§ 3. OBSERVATIONS AND ANALYSIS

Both the lines λ_{3247} and λ_{3274} were found to be simple doublets each consisting of two components with intensity-ratio visually estimated as 1.5 : 1. (The theoretical ratio is 1.66 : 1, which is some 10 per cent greater. Such a difference can hardly be distinguished visually and we may safely assume that the theoretical intensities are those which actually occur.) In both lines the weaker component is towards the violet. The separation in λ_{3247} is $379 \times 10^{-3} \text{ cm}^{-1}$, and in λ_{3274} it is $405 \times 10^{-3} \text{ cm}^{-1}$, the error in each case not being much greater than $1 \times 10^{-3} \text{ cm}^{-1}$.

Although Ritschl's lines were broadened, the separations he reports are very close to those given here. In table 1 are the separations according to Sibaiya, Ritschl and the authors.

Table 1

Wave-length	Separation (cm. $\times 10^{-3}$)		
	Sibaiya	Ritschl	Authors
3247	366	371	379
3274	406	405	405

Attention may be drawn to the fact that Sibaiya's lines were completely reversed and Ritschl's lines somewhat broadened, while our lines were quite sharp. Only λ_{3247} seems to be affected by the reversal, the separation of the components diminishing with increasing amount of reversal.

In Ritschl's measurements the uncertainty due to the widths of the lines was such that he predicted a separation of $394 \times 10^{-3} \text{ cm}^{-1}$ for λ_{3247} . This value he accepted for the purpose of analysis and he was unable to show that it is actually incorrect. This has led him to assign an incorrect value to the structure of the $3d^{10}4p \ ^2P_{1/2}$ term. Schüler and Schmidt also prove that this term is wrongly analysed, from a consideration of the structures in λ_{5700} and λ_{5782} . Ritschl's measurements lead to a structure of $390 \times 10^{-3} \text{ cm}^{-1}$ for the ground term.

In figure 2 are drawn the lines reported here and those studied by Schüler and Schmidt, the latter being dotted. The broken line λ_{5105} is one of those measured by Ritschl and utilized by Schüler and Schmidt in deriving a value for the nuclear magnetic moment. The dotted lines exhibit isotope displacement, and from their structures Schüler and Schmidt conclude that the hyperfine-structure separations in the $3d^{10}4p \ ^2P_{1/2}$ level are respectively $28 \times 10^{-3} \text{ cm}^{-1}$ for the more abundant isotope

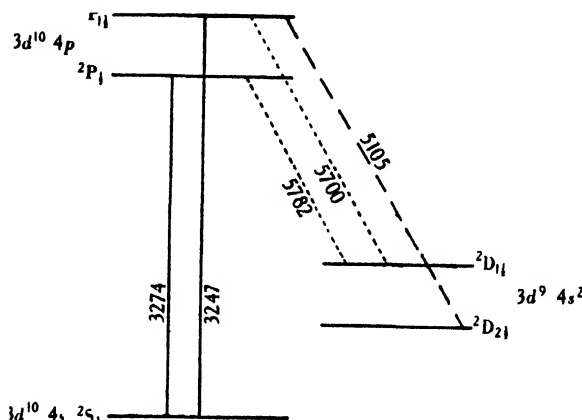


Figure 2

(63) and $29 \times 10^{-3} \text{ cm}^{-1}$ for the less abundant isotope (65). The isotope abundance ratio is about 2.1 : 1. The mean interval factor of this term for the two isotopes, given independently by Ritschl, is $28 \times 10^{-3} \text{ cm}^{-1}$. The lines involved are in both cases highly complex and incompletely resolved. A careful examination of the structure diagram given by Schüler and Schmidt for λ_{5782} , which is more completely resolved than λ_{5700} , shows that while the value $28 \times 10^{-3} \text{ cm}^{-1}$ is certainly correct for the lighter isotope, some uncertainty exists as to whether the separation for the heavier isotope actually differs by the very small amount suggested; if the nuclear magnetic moments are different, the small variation will be expected. We shall assume here that the structure in the $3d^{10}4p \ ^2P_{1/2}$ term is $28 \times 10^{-3} \text{ cm}^{-1}$ for both the isotopes, and it is quite certain that no appreciable error is introduced into our analysis of the structure of the ground term, since this does not exhibit a measurable isotope displacement, owing no doubt to the fact that the d electron shell is here complete.

The analysis of the structure of λ_{3274} is shown in figure 3. The arrow heads, drawn at the centres of gravity of each close unresolved pair of components, repre-

sent the positions of the observed lines. On the basis of this analysis the separation in the $3d^{10}4s\ ^2S_{\frac{1}{2}}$ ground term is $395 \times 10^{-3} \text{ cm}^{-1}$

Figure 4 shows the analysis for the line $\lambda 3247$. In this case the lower term is made to have the separation $395 \times 10^{-3} \text{ cm}^{-1}$ already derived, and a value adopted for the interval factor in the upper term which will make the centre of gravity of the two components $379 \times 10^{-3} \text{ cm}^{-1}$ apart. It can be justifiably assumed that the interval rule holds in the upper term, since deviations will only introduce a second order

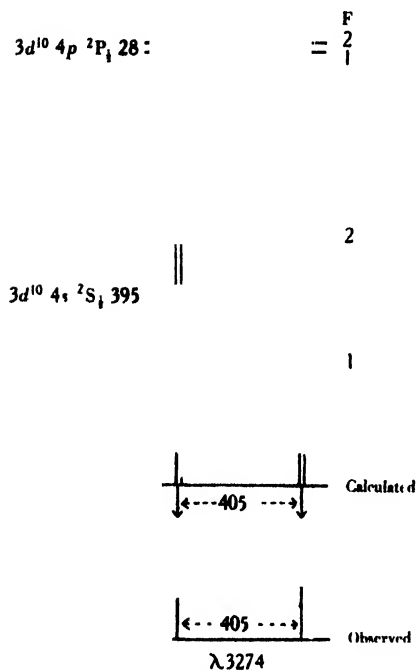


Figure 3

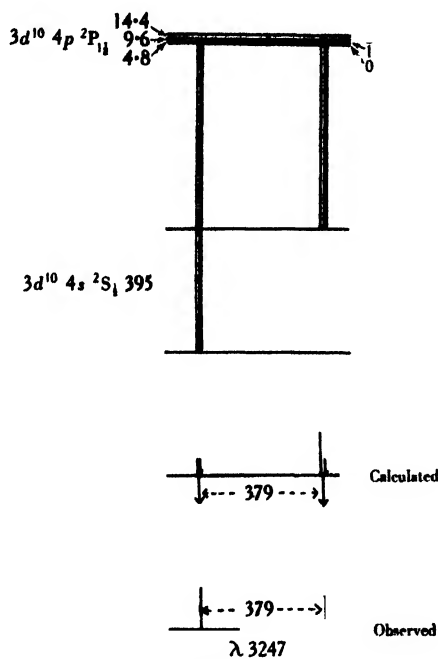


Figure 4

effect. The interval factor calculated by this method for the upper term, $3d^{10}4p\ ^2P_{\frac{1}{2}}$ is $4.8 \times 10^{-3} \text{ cm}^{-1}$. This is in remarkably exact agreement with that found by Schüller and Schmidt for the same term by means of the line $\lambda 5700$. These authors give the separation as $4.8 \times 10^{-3} \text{ cm}^{-1}$ for the more abundant isotope and estimate $5.0 \times 10^{-3} \text{ cm}^{-1}$ as the separation for the less abundant isotope. The difference between these can be neglected. The close agreement for the structure derived from quite independent lines confirms the analysis made by Schüller and Schmidt and by us, and in particular it shows that the value $395 \times 10^{-3} \text{ cm}^{-1}$ for the ground term is very accurate.

The interval factors for the terms we have observed are shown in table 2.

Table 2

Term	Interval factor ($\text{cm}^{-1} \times 10^{-3}$)
$3d^{10}4s\ ^2S_{\frac{1}{2}}$	197.5
$3d^{10}4p\ ^2P_{\frac{1}{2}}$	14.0
$3d^{10}4p\ ^2P_{\frac{1}{2}}$	4.8

The differences in λ_{3247} in table 1 can be accounted for, if it is assumed that there is preferential absorption of the component $\Delta F=2 \rightarrow 1$. Thus it is the line coming from the higher F level of the term with higher J that is more absorbed.

§ 4. THE NUCLEAR MAGNETIC MOMENT

As has previously been pointed out, the ground state $3d^{10}4s^2 {}^2S_{\frac{1}{2}}$ is well suited for the calculation of the nuclear magnetic moment of copper, since the term configuration is in effect that of a single penetrating electron. The theory of Goudsmit⁽⁹⁾ and of Fermi and Segré⁽²⁾ can therefore be applied with confidence. Furthermore, the state, being spherically symmetrical, nuclear quadrupole moment does not enter into the calculation. This is not true for $3d^9 4s^2 {}^2D_{\frac{1}{2}}$ and $3d^9 4s^2 {}^2D_{\frac{3}{2}}$, which Schüler and Schmidt use for the calculation of μ , employing the analysis of the lines $\lambda 5700$, 5782 and 5105 . Since 2.44 is the nuclear magnetic moment μ calculated by Schüler from Ritschl's value, $390 \times 10^{-3} \text{ cm}^{-1}$, for the ground term, replacing the latter by our measurement, $395 \times 10^{-3} \text{ cm}^{-1}$ gives $\mu = 2.47$ nuclear magnetons.

The magnetic moments calculated by Schüler and Schmidt from the 2D terms are given in table 3.

Table 3

Term	Mean μ	μ (${}^{63}\text{Cu}$)	μ (${}^{65}\text{Cu}$)
$3d^9 4s^2 {}^2D_{\frac{1}{2}}$	2.56	2.52	2.64
$3d^9 4s^2 {}^2D_{\frac{3}{2}}$	2.5		

The mean value for the $3d^9 4s^2 {}^2D_{\frac{1}{2}}$ term has been obtained by taking into account the abundance ratio and weighting according to this. We consider that the above data definitely establish that the nuclear magnetic moments of the two isotopes differ and are in the ratio of $1.048 : 1$. However, the value we give for the mean μ , i.e. 2.47 , is probably more correct. This is due partly to the absence of perturbation and partly to the fact that a penetrating s electron is involved. This latter point is important, since the formula for the magnetic moment is likely to be more correct here. If we adopt the ratio $1.048 : 1$ for the two isotopes, we can derive magnetic moments for them. Thus we have finally the values shown in table 4.

Table 4

Term	Mean μ observed	μ (${}^{63}\text{Cu}$) calculated	μ (${}^{65}\text{Cu}$) calculated
$3d^{10}4s^2 {}^2S_{\frac{1}{2}}$	2.47	2.43	2.54

§ 5. ACKNOWLEDGEMENT

The Lummer plate and the optical parts of the spectrograph were purchased with the aid of a grant made to one of us (S. T.) by the Government Grants Committee of the Royal Society.

We wish to thank Dr Simeon for recalculating the dispersions of the Lummer plate.

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THE SPECIFIC HEAT OF NICKEL FROM 100° C. TO 600° C.

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ABSTRACT. The {specific-heat, temperature} curves for four different types of nickel have been determined, and the effects of method of manufacture, heat treatment, and chemical composition have been ascertained. The results, together with those obtained by previous investigators, are reviewed, and an attempt made to evaluate the most probable $\{C_p, T\}$ curve for nickel for the temperature range 100° C. to 600° C.

§ 1. INTRODUCTION

STONER⁽¹⁾ has made an analysis of certain experimental values for the specific heat of nickel with a view to obtaining some indication of the dependence of electronic energy on temperature and magnetization for a ferromagnetic material. The treatment followed by him is, briefly, as follows. After subtraction of a calculated dilatation correction ($C_p - C_v$) from the measured specific heat C_p , to obtain C_v , C_v is considered as the sum of three terms, so that $C_v = C_Q + C_E + C_M$. C_Q is the main contribution to the specific heat, connected with lattice energy, represented by a Debye expression and calculated when a reasonable estimate of the characteristic Debye temperature Θ_D has been made. C_E and C_M together comprise an electronic specific heat, C_M being the part of it associated with the spin orientation of the electrons and hence with the magnetization, while C_E is associated with changes in translational state.

Theoretical estimates of C_E are made, and from low-temperature measurements of specific heat ($C_Q + C_M$) is found by difference, as $(C_v - C_E)$; the Debye temperature Θ_D governing the values of C_Q can be most accurately deduced from specific heats at low temperatures, where C_M is small, by comparison, and an approximate estimate of its value is sufficient. The value of Θ_D then gives values of C_Q for all temperatures and so leads to values for C_M . From C_M estimates of the molecular field coefficient are made for comparison with those found by other methods.

The object of the present paper is to present the results of new precise determinations of the specific heat of nickel which, while in general confirming the values previously adopted, serve as additional criteria for the choice of values of the specific heat in cases in which previous results are not in sufficiently good agreement to enable reliable theoretical deductions to be made.

Although almost all previous investigators claim an accuracy of at least 2 per cent in the measurement of specific heat, comparison of their results shows discrepancies in excess of that amount. The lack of agreement has been ascribed to

differences in the degree of purity, method of manufacture, metallographic structure and heat treatment of the specimens. On the other hand, no investigator has studied the effect of impurities using identical apparatus and technique. Consequently, it appeared probable that some part of the discrepancies were, in fact, experimental error.

Above the Curie point the C_M term vanishes and the specific heat C_v is made up of two terms C_Q and C_E . As the lattice energy contribution C_Q is of the order of 80 per cent of the measured value C_p , relatively small errors in C_p give rise to large percentage errors in the value of C_E obtained by difference. The effect of impurities on C_p should be relatively small, yet some of the greatest discrepancies between the results of previous workers occur in the region above the Curie point. Using four different types of nickel prepared in a variety of ways, we have investigated this part of the {specific-heat, temperature} curve very carefully and find that any differences which can be ascribed to the presence of impurities or insufficient annealing are of the order of our experimental error, namely 2 per cent.

Impurities undoubtedly affect the Curie temperature, for instance 1 per cent of cobalt raises it by about 12° C. whereas the addition of 1 per cent of silicon lowers it by 70° C. It has been suggested that the shape of the {specific-heat, temperature} curve in the neighbourhood of the Curie point is very sensitive to the presence of impurities, and that for perfectly pure nickel, free from strain, the curve should drop very steeply to a minimum just above the Curie point, indicating that the co-ordination of electron spin even for small groups of atoms vanishes completely at the Curie point. On the other hand, by analogy with superlattice formation, local co-ordination above the Curie point would be expected, and this would give rise to a tail on the {specific-heat, temperature} curve. Our experimental technique is better adapted to the investigation of the rapid variation of C_p in the Curie-point region than any previously used, as it permits continuous measurements of instantaneous specific heat to be made as the temperature of the specimen is varied. All the specimens examined, irrespective of their heat treatment, gave {specific-heat, temperature} curves in which no sharp minimum occurred just above the Curie point and it is concluded that this feature of the curve is not particularly sensitive to traces of impurity or variations in heat treatment.

§ 2. EXPERIMENTAL ARRANGEMENTS

Method. The apparatus and technique employed were identical with those used in investigations on superlattice transformations in the alloys Cu_3Au ⁽³⁾ and CuZn ⁽⁴⁾, and has been fully described elsewhere⁽⁵⁾. The principle is as follows. The specimen is heated electrically *in vacuo* at about 1.5° C. per minute inside a copper enclosure which is heated independently at the same rate. The temperature-difference between specimen and enclosure is kept small, namely $\pm 0.5^\circ \text{C}$. A small differential heating or cooling-rate of the specimen relative to the enclosure is measured by observing the deflection of a sensitive galvanometer which is energized by a differential thermocouple. Rapid changes in specific heat appear as changes in the differential

heating-rate, and by taking readings of the galvanometer at half-minute intervals data are obtained from which the instantaneous specific heat may be calculated at temperature-intervals of 1°C . if desired.

In the temperature-range from 400°C . to 600°C . the specific-heat measurements have been supplemented by experimental measurements of the differences of total energy content. A copper voltameter is used to integrate the current which is supplied to raise the temperature of the specimen from 400°C . to 600°C . The current is passed intermittently so that the temperatures of specimen and enclosure never vary by more than $\pm 0.3^{\circ}\text{C}$. These measurements serve as a reliable check on the direct measurements of the {specific-heat, temperature} curve and will be discussed in § 3.

Material. Four types of nickel designated I, II, III and IV have been examined. The chemical analysis is given in table 1. Samples II and III are very pure. I has a low Curie point, and IV a high Curie point. The selection is thus reasonably representative.

Table 1

Material	Impurities (per cent)							
	Iron	Cobalt	Carbon	Copper	Man- ganese	Silicon	Sulphur	Oxygen
I Commercial	0.15	0.45	—	—	0.03	0.19	—	—
II Mond pellets	0.031	Nil	0.025	0.007	—	—	0.004	—
III Powder	0.04	Nil	trace	—	—	—	—	trace
IV Cathode	0.01	0.41	—	0.04	—	—	—	—

The specific-heat specimens were prepared in the form of closed hollow cylinders 1 in. in diameter and $1\frac{1}{4}$ in. long, and weighed approximately 100 g. Sample I was machined from a forged bar $1\frac{1}{8}$ in. in diameter and is typical of material classed as commercially pure nickel. Samples II, III and IV were prepared from raw material very kindly provided by the Mond Nickel Company through the agency of Mr W. T. Griffiths and Dr L. B. Pfeil. The analyses given for these materials refer to the raw material before melting or sintering and were supplied by the Mond Nickel Laboratories. Samples II and IV were melted in a high-frequency furnace in high vacuum, the pressure being less than 10^{-3} mm. of mercury, and then hammered to a suitable shape before being machined. Sample III was prepared by sintering a block of pressed powder *in vacuo* at 900°C ., that is to say, the material was not melted. The sintered block was slightly porous, having an apparent density 85 per cent that of melted nickel. It machined quite satisfactorily. Except where the contrary is stated the specific-heat specimens after being machined were heated *in vacuo* to 900°C . and cooled at 1°C . per minute to room-temperature before measurements were made.

Accuracy. In a previous paper⁽⁵⁾ the errors likely to arise in specific-heat measurements made by the method used in this investigation have been discussed at length for the temperature range 100°C . to 400°C . Absolute errors arise in the determination of power input of ± 0.2 per cent, of heating rate ± 0.4 per cent and

from faulty experimental conditions due to uncertainties regarding the e.m.f. of the differential thermocouple ± 0.2 per cent. Observational errors are found to be within the limits of ± 0.75 per cent, but these can substantially be eliminated by taking a large number of experimental points. Consequently it is reasonable to conclude that the maximum absolute error will not exceed ± 1 per cent, with a probable error of ± 0.5 per cent. This claim is made for results recorded in this paper for the region 100° C. to 400° C. with the exception of a 10° C. interval immediately above the Curie point. In this region the specific heat falls very rapidly, and errors in determining the differential heating rate (which can be neglected in general) become appreciable, with a consequent increase in the observational error to about twice the normal value, viz.: ± 1.5 per cent. Again these errors have been minimized graphically from a large number of experimental points, and we estimate the absolute error in this region to be within ± 1.5 per cent.

In the region from 400° C. to 600° C. the accuracy falls off rapidly, primarily owing to uncertainty regarding the e.m.f. of the differential thermocouple. The experimental method involves the assumption that the e.m.f. of the differential thermocouple is known when specimen and enclosure are at the same temperature. Experience indicates that, even after special precautions have been taken in the preparation of the thermocouples, no two thermocouples give exactly the same e.m.f. at the same temperature, nor is the e.m.f. exactly reproducible. For a true difference in temperature of 1° C. between specimen and enclosure the corresponding radiation correction amounts to 1.6 per cent of the specific heat at 400° C. and 5 per cent at 600° C. Consequently, the e.m.f. for zero temperature-difference must be known and reproducible to an amount corresponding to 0.2° C. at 600° C., i.e. 1 part in 3000, in order that errors in specific heat due to this cause alone shall not exceed ± 1 per cent. Our experience is that the limit of accuracy of the differential thermocouple is of this order at 600° C. Observational errors also increase in consequence of experimental difficulties encountered in heating the copper enclosure at a steady rate at high temperatures.

In order to minimize errors due to these difficulties as far as possible, we have supplemented specific-heat measurements by measurements of differences of energy-content from 400° C. to 600° C. Duplicate measurements have been made with the differential thermocouple reversed and with different thermocouples. In this way errors due to choice of an incorrect e.m.f. for zero temperature-difference between specimen and enclosure are eliminated, and only errors due to lack of reproducibility remain. The measurements are independent of any precise determination of the heating rate, and agree for a definite arrangement of the differential thermocouple to within ± 0.4 per cent. The absolute accuracy of the mean values of the energy-content difference is estimated to be within ± 1 per cent. As a check the change in energy-content of copper from 400° C. to 600° C. has been determined. The result, 20.79 cal./g., agrees with that found by Jaeger by the calorimeter method, 20.60 cal./g. to within 1 per cent.

The experimentally determined values of specific heat have been used to give the shape of the {specific-heat, temperature} curve, and the actual curves have been

Table 2
nickel (cal./g. per

Temperature (° C.)	0	10	20	30	40	50	60	70	80	90	100
I II III IV Mean of II and III	Commercially pure nickel Vacuum melted pure Mond Pressed powder Cathode nickel										
I II III IV Mean of II and III	1128 1125 1121 1128 1123	1143 1138 1136 1140 1137	1156 1149 1146 1154 1147	1169 1160 1158 1165 1159	1181 1170 1170 1177 1170	1191 1180 1181 1187 1180	1202 1188 1191 1196 1190	1210 1197 1199 1204 1198	1220 1205 1207 1213 1206	1230 1214 1215 1222 1214	
I II III IV Mean of II and III	1240 1225 1225 1231 1225	1251 1236 1236 1243 1236	1262 1249 1248 1256 1248	1275 1262 1260 1269 1261	1287 1279 1275 1283 1277	1300 1294 1289 1296 1292	1315 1310 1303 1310 1307	1330 1324 1318 1325 1321	1349 1340 1334 1340 1337	1368 1355 1348 1354 1352	
I II III IV Mean of II and III	1386 1371 1363 1369 1367	1404 1388 1379 1385 1384	1424 1407 1405 1400 1406	1452 1438 1426 1419 1427	1460 1454 1454 1441 1454	1322 1402 1495 1470 1493	1292 1420 1373 1534 1396	1279 1322 1308 1335 1315	1270 1302 1280 1294 1291	1266 1282 1271 1275 1276	
I II III IV Mean of II and III	1263 1269 1264 1265 1267	1260 1261 1260 1260 1261	1258 1256 1257 1256	1256 1252 1255 1254	1256 1251 1253 1252	1256 1251 1252 1251	1257 1253 1252 1252	1258 1257 1252 1254	1259 1260 1254 1257	1261 1265 1256 1260	
I II III IV Mean of II and III	1263 1270 1259	1265 1276 1264	1270 1281 1269	1274 1287 1275	1279 1293 1281	1283 1299 1286	1287 1305 1293	1292 1311 1301	1297 1317 1307	1302 1322 1315	1306 1328 1324
Mean of II and III	1265	1270	1275	1281	1287	1292	1299	1306	1312	1318	1326

drawn to give the correct energy-contents, see table 2. We estimate that the maximum absolute error in specific heat increases from ± 1 per cent at 400° C. to ± 2 per cent at 600° C.

The temperature measurements were made with a thermocouple which was regularly checked against a platinum-platinum-rhodium thermocouple. This standard couple was calibrated very carefully⁽⁵⁾. The temperature scale is considered accurate to $\pm 1.5^\circ$ C.

The effect of eddy currents in the nickel specimen produced by the alternating current used to heat the copper enclosure has been examined. The specific-heat curve of a sample of soft iron was measured first under a.-c. heating and secondly under d.-c. heating. No difference could be detected. It is concluded that the various copper screens incorporated in the apparatus effectively shield the specimen.

§ 3. EXPERIMENTAL RESULTS

Annealed material. Four experiments were carried out on each type of nickel, and the specific heat was calculated at about 25 different temperatures for each experiment. These 100 or so points were plotted and the best curve was drawn through them; the majority of the points lay within 0.5 per cent of this mean curve in the region 100° C. to 400° C. The values of specific heat given in tables 2 and 3 from 100° C. to 400° C. were read off from these mean curves.

Table 3. Curie-point region
Specific heat (cal./g. per ° C.) $\times 10^4$

Temperature (° C.)	I	II	III	IV	Mean of II and III
325	1437	—	—	—	—
330	1452	1428	1426	1419	1427
335	1474	—	—	—	—
339.5	1510	—	—	—	—
340	1460	1454	1454	1441	1454
342	1400	—	—	—	—
345	1358	1470	1471	1454	1470
350	1322	1492	1495	1470	1493
352	—	1504	1508	—	1506
354	—	1520	1524	1487	1522
356	—	1543	1547	1498	1545
357	—	1562	1563	—	1562
357.5	—	—	1576	—	—
358	—	1586	1470	1511	1580
359	—	1460	1395	—	—
360	1292	1420	1373	1534	1396
361	—	—	—	1550	—
362	—	1384	1352	1578	1368
363	—	—	—	1600	—
364	—	1364	1338	1420	1351
365	—	—	—	1390	—
370	1279	1330	1308	1335	1319
375	—	1312	1290	1310	1301

Four determinations of differences in the energy-content were made on each material for the temperature range 400° C. to 600° C. The mean results obtained are given in table 4 together with the mean deviations.

Table 4

Sample	Difference of energy-content from 400° c. to 600° c. (cal./g.)	Deviation
I	25.45	0.05
II	25.58	0.14
III	25.42	0.19
IV	25.64	0.02
Mean	25.52	

These data and direct specific-heat measurements were combined to give the values of specific heat recorded in table 3 for the range 400° c. to 600° c., but measurements of specific heat were not made for specimen IV in this range.

The mean results for each type of nickel in the neighbourhood of the Curie-point (330 to 380° c.) are plotted in figure 1.

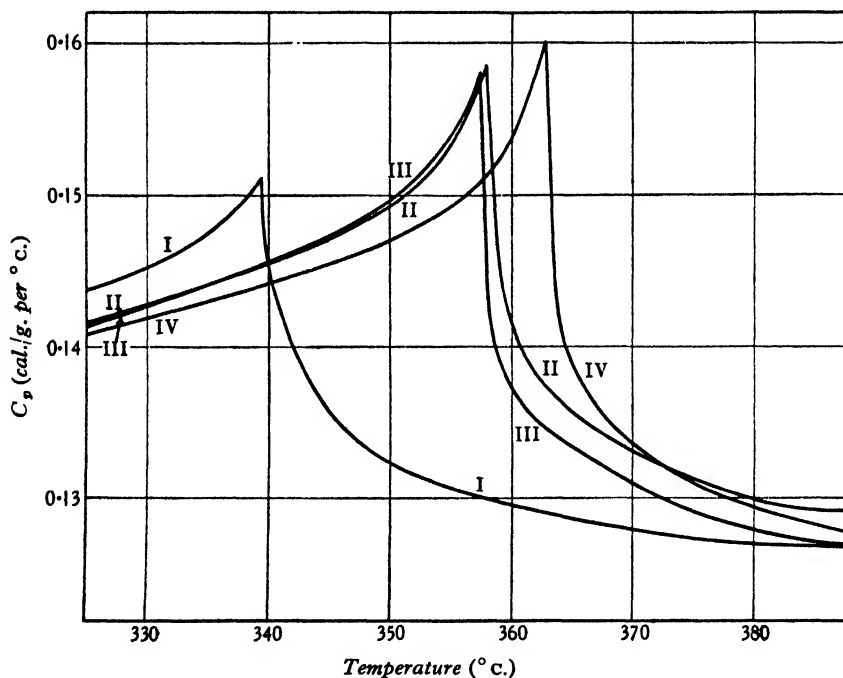


Figure 1.

§ 4. DISCUSSION OF EXPERIMENTAL RESULTS

Samples II and III are both of high purity, i.e. 99.9 per cent nickel, and their {specific-heat, temperature} curves are identical within the limits of experimental error over the greater part of the temperature range; see table 2.

Allowing for the slight difference of about 1° c. between the Curie points of samples II and III, see figure 1, there is a difference decreasing from 2 per cent

to 1 per cent in the range 360° C. to 390° C.; as this is of the same order as the experimental error expected in the Curie-point region, it is concluded that the difference in behaviour between the two materials even in this region is quite small.

Sample IV gives similar results to samples II and III from 400° C. to 600° C., table 4; from 100° C. to 320° C. the values of C_p are about 0.5 per cent higher. The Curie point is much higher, namely 363° C., owing to the presence of cobalt. Allowing for this difference in Curie point it will be found that curve IV can be superposed almost exactly on curve III in the Curie-point region, figure 1. Consequently the addition of 0.4 per cent of cobalt has not materially modified the shape of the tail of {specific-heat, temperature} curve.

Sample I, containing appreciable quantities of impurities, in particular silicon, has a low Curie temperature, namely 340° C., and a low maximum specific heat, namely 0.152 cal./g. per ° C. If this curve is transposed 18° C., the difference in Curie temperature between samples I and III, it will be found to lie between curves II and III, so that apart from the decreased maximum specific heat the behaviour in the Curie-point region is not markedly different from that of samples II, III and IV. In the region below the Curie point the values of C_p lie consistently higher than for the other samples; see table 2. This is to be expected since the contribution to C_p by the magnetic transformation is restricted to lower temperatures. A comparison of the total difference of energy-content for the temperature range of 200° C. below the Curie point has been made for samples I and II. The results are 26.05 cal./g. for I and 26.43 cal./g. for II; so that the total change is not great.

From 400° C. to 550° C. the values of C_p for sample I are in satisfactory agreement with those for the other samples. Above 550° C. the results are lower by about 1.5 per cent, suggesting that the rate of rise of C_p in this region is somewhat slower than for the pure materials.

From this survey of the experimental results on annealed material we conclude that over the range of compositions tested the presence of impurities does not materially affect either the shape of the tail of the {specific-heat, temperature} curve in the neighbourhood of the Curie point or the values of the specific heat above the Curie point. On the other hand, both the Curie point and the maximum specific heat are sensitive to the presence of impurities.

§ 5. INFLUENCE OF METHOD OF PREPARATION OF SPECIMEN

Melting procedure. Samples I, II and III were produced in three distinct ways. The commercially pure nickel I would be melted in air, cast into an ingot of cross section about 4 in. square, forged, and then rolled to a diameter of 1½ in. The Mond nickel II was melted *in vacuo* and the reduction in diameter by forging was in this case only about 10 per cent. Sample III was prepared from powder of particle-size approximately 10^{-2} mm. and was sintered at 900° C., a temperature well below the melting point of nickel (1450° C.) so that very little grain growth could take place. In view of the experimental results obtained, it is clear that neither the tail on the

{specific-heat, temperature} curve nor the values of C_p above the Curie point are markedly sensitive to the mode of manufacture, crystal-size or the like.

Effect of heat treatment. The results listed in table 3 were obtained on the different samples heat-treated in an identical manner. We have carried out a number of experiments on samples III and IV to determine whether variation in heat treatment produced any changes in the C_p curve.

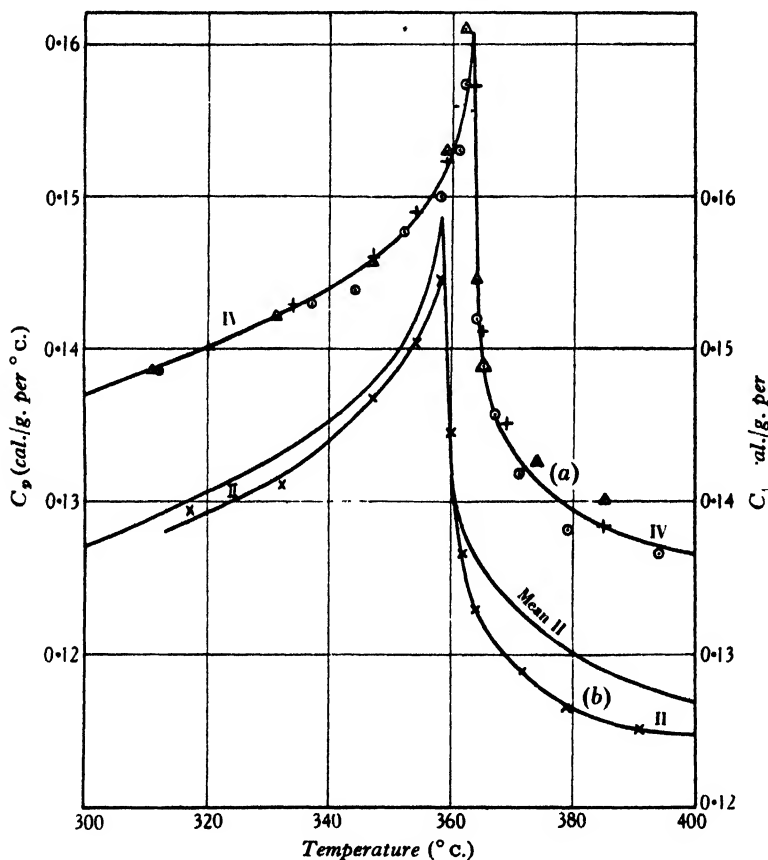


Figure 2. \odot , IV quenched 700°C .; $+$, IV cooled from 600°C . at 1°C./min. ; \triangle , IV cooled 1°C./min. , from 900°C .; \times , II annealed 300 h. at 350°C .

Two specimens of cathode nickel, sample IV, were prepared. One was cooled from 900°C . at $1^{\circ}\text{C. per minute}$, and the other was quenched from 700°C . in water. The {specific-heat, temperature} curves were taken, and an additional curve was taken on the quenched sample after it had been cooled at $1^{\circ}\text{C. per minute}$ from 600°C . The experimental points obtained are shown in figure 2 (a) for the Curie-point region. Within the limits of error they all fall on the mean curve. A specimen of vacuum-melted Mond nickel, sample II, was annealed at 350°C . for 300 hours *in vacuo*. The {specific-heat, temperature} curve obtained is shown in figure 2 (b) together with the mean curve for sample II. The change, if any, produced by this

annealing treatment is very small. We conclude from the above experiments that the {specific-heat, temperature} curves of pure nickel are not particularly sensitive to heat treatment.

It is conceivable that our experimental method might smooth out any minimum on the {specific-heat, temperature} curve. This point has been checked experimentally in connexion with another investigation. A specimen of iron was fitted with an insert of zinc weighing about 1 g., which was 1 per cent of the total weight of the specimen. The {specific-heat, temperature} curve was determined and at the melting point of zinc a sharp maximum was observed. The anomaly in the {specific-heat, temperature} curve was restricted to a temperature-interval of about 4° C. The tail on the specific heat curves, figure 1, which stretches over some 30° C., is thus a genuine property of the samples under investigation.

§ 6. COMPARISON OF EXPERIMENTAL RESULTS WITH PREVIOUS RESULTS

General. Table 5 gives the values of C_p (specific heat per gram-atom) found by various investigators for the temperatures given in degrees absolute in column 1. The estimated accuracy given by each investigator is also tabulated.

Table 5
Atomic heat C_p (cal./gram-atom per ° C.)

Temperature (° K.)	Lapp	Grew	Ahrens	Moser	Klink- hardt	Sykes and Wilkinson	Transposed Sykes and Wilkinson	Most probable values
350	6·51	6·60	6·52	6·46	—	—	—	6·51
400	6·75	6·86	6·84	6·69	—	6·78	—	6·76
450	7·05	7·14	7·14	7·04	—	7·07	—	7·07
500	7·42	7·49	7·52	7·48	—	7·48	—	7·47
550	7·88	7·90	8·01	7·78	—	7·82	—	7·83
600	8·45	8·55	8·72	8·28	—	8·34	8·36	8·37
610	8·67	8·79	8·95	8·43	—	8·49	8·55	8·49 (8·57)
620	8·95	9·05	9·18	8·62	—	8·69	8·78	8·69 (8·80)
622	9·04	9·12	9·22	8·66	—	8·74	8·89	8·74 (8·88)
624	9·13	9·18	9·28	8·80	—	8·80	9·02	8·80 (8·99)
626	9·23	9·25	9·36	8·87	—	8·89	9·28	8·89 (9·13)
628	—	Interpolated		—	—	—	—	9·02 (8·61)
630	7·80	8·70	8·25	8·22	—	9·28	8·12	9·28 (8·20)
635	7·42	8·25	8·18	7·93	—	8·04	7·87	8·04 (7·88)
640	7·43	7·98	8·06	7·72	—	7·87	7·74	7·87 (7·72)
650	7·44	7·70	8·00	7·48	7·31	7·62	—	7·50
700	—	—	—	7·32	7·35	7·37	—	7·35
750	—	—	—	7·31	7·42	7·37	—	7·37
800	—	—	—	7·33	7·51	7·48	—	7·44
850	—	—	—	7·36	7·68	7·66	—	7·50 (7·57)
Estimated error (per cent)	± 2	± 2	± 2	± 0·5	± 3	± 1 to ± 2		

The purity of the samples used was as shown in table 6. We shall compare the results obtained on these materials with the mean result for samples II and III. All investigators used an aneroid method; the energy necessary to raise the specimen over a small temperature interval of about 2° C. was determined. The mean specific heat over the temperature-interval was assumed equal to the instantaneous specific

heat at the mean temperature. Lapp, Grew and Ahrens used wires which were heated electrically by the passage of current. Klinkhardt heated a massive specimen by means of electron bombardment. In both these methods the temperature of the enclosure surrounding the specimen was held constant throughout the course of the experiment, and a radiation correction had to be made for loss of heat by the specimen. Moser heated his specimen electrically in a tightly fitting silver calorimeter, and arranged that the temperature of the surroundings should increase at substantially the same speed as the specimen. In this way he reduced the radiation correction. Grew, Ahrens and Klinkhardt carried out their experiments *in vacuo* to reduce heat losses, Moser used a reduced pressure of argon, and Lapp appears to have worked with air at atmospheric pressure.

Table 6

Investigator	Material	Impurities (per cent)						
		Iron	Copper	Carbon	Silicon	Mag- nesium	Man- ganes	Sulphur
Lapp	Nickel wire	0.19	0.06	0.04	0.02	0.18	—	—
Grew	Nickel wire (Hilger)	Impurity 0.03 per cent						
Ahrens	Wire, carbonylnickel	Stated to be of high purity						
Ahrens	Wire, Rein nickel	0.2	0.07	—	0.04	—	0.18	—
Moser	Mond nickel	0.1	—	—	0.003	0.07	—	0.003
Klinkhardt	Vacuum melted nickel	—	—	—	—	—	0.5	—

The temperature range, 350° K. to 610° K. Ahrens's results, given in table 5, refer to his carbonyl nickel. Klinkhardt's results at low temperatures are not included as his material had a very low Curie point owing to the presence of manganese. The agreement from 350° K. to 610° K. is satisfactory; it is ± 1.5 per cent, which is within the range of estimated errors provided the results of Ahrens are not considered. For reasons which will be given later in connexion with the range 650° K. to 850° K., it is highly probable that his results are high throughout the major portion of the temperature range 350° K. to 650° K. by an amount greater than 2 per cent.

In the ninth column of table 5 we list probable values which are obtained by giving each experimental method an equal weight independent of the number of the determinations made by that method; thus we give Lapp and Grew a weight of 1, Moser and our own results, column 7, a weight of 2. Ahrens's results are neglected.

The Curie-point region, 610° C. to 650° K. The results obtained are shown graphically in figure 3. Apart from the one result obtained by Lapp, all the curves agree in showing a well-defined tail. The sharp minimum found by Lapp cannot be attributed to high purity (in view of the analyses), or to an especially prolonged heat treatment, since none is specified. It is conceivable that the wire sample had a pronouncedly fibrous structure which differentiated it from material used by other investigators, yet Grew and Ahrens, who also used wire, did not confirm Lapp's result.

In our opinion the wire method is not particularly suitable for high-temperature measurements of specific heat in view of the relatively high surface-to-mass ratio, which necessitates large radiation corrections. In Lapp's measurements at the Curie point this correction amounted to 18 per cent though in our experiments it seldom exceeded 0.5 per cent. The correction is sensitive to variation in emissivity and gas pressure; neither Grew, Lapp nor Ahrens give any precise details regarding the methods adopted to keep the gas pressure constant. With wires fluctuations in gas pressure above 5×10^{-3} mm. of mercury will affect the radiation correction to an appreciable extent. Additional difficulties arise from the necessity for controlling the

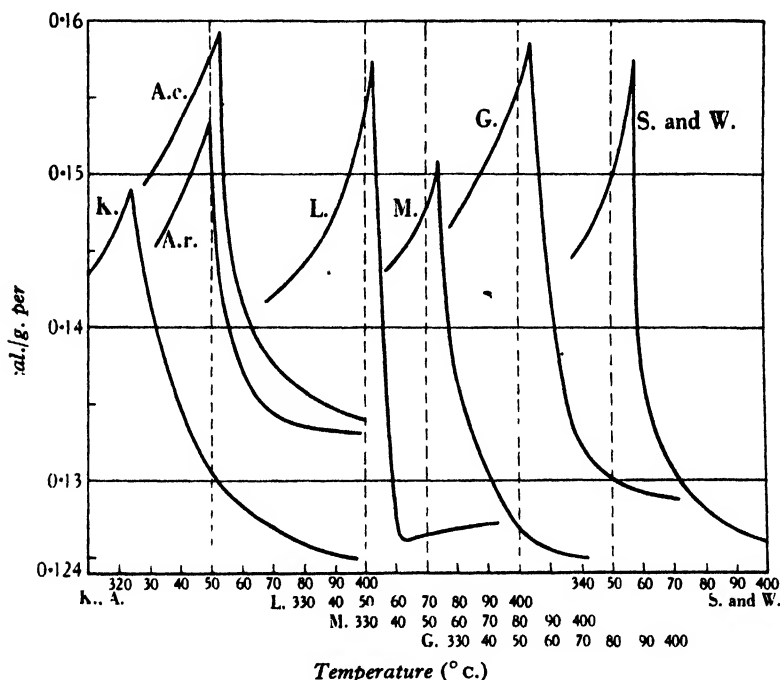


Figure 3.

temperature of the surroundings carefully, a change of 0.005° C. per minute being important. These considerations throw doubt on Lapp's result and on the results obtained by the wire method in general. It is significant that in the range from 400° C. to 500° C., figure 4, the deviations in the results obtained by the three different methods used by Klinkhardt, Moser, and Sykes and Wilkinson are much smaller than the deviations in the results obtained by different investigators using the wire method.

As we have previously pointed out, our results in figure 1 indicate that the tail on the {specific-heat, temperature} curve is not sensitive to the presence of impurity or normal variations in heat treatment. Ahrens's results on carbonyl nickel (A.c.), figure 3, and Rein nickel (A.r.) of widely differing composition, confirm this conclusion.

The variation in Curie point found by different observers is much greater than the probable experimental errors and is no doubt caused by the presence of impurities. Whilst Lapp's impure nickel and Ahrens's Rein nickel give relatively high Curie points, indicating that some of the impurities must be self-compensating, their effect on the magnetic properties is not certain and the results obtained with these materials together with those obtained with Klinkhardt's are considered to be unreliable. The samples which are known to be reasonably pure, namely carbonyl iron (Ahrens), Mond nickel (Moser), Hilger nickel (Grew), and our samples II and III, have Curie points at 353°C. , 354°C. , 358°C. and 357.5°C. respectively. The variation is outside the limits of our experimental error and it appears that the residual impurities present in the samples still exert an appreciable effect. For comparison purposes the ratio of the maximum specific heat to the specific heat at 400°C. is a reasonable criterion, since it eliminates to a great extent variations due to differing Curie temperature and also errors peculiar to each set of measurements. This ratio is 1.19 (Ahrens), 1.20 (Moser), 1.23 (Grew) and 1.25 from our own measurements. The differences are relatively small in view of the experimental difficulties encountered in this region in consequence of the rapid change in specific heat. Our value is the highest which is to be expected since the experimental method is likely to give the nearest approximation to the maximum specific heat.

The differences in Curie point render discussion of the results in the range 610°K. to 640°K. difficult. If our curve, column 7 of table 5, Curie point 630°K. , is transposed* to a position 4°K. lower, the values given in column 8 are obtained, and these are in reasonable agreement with those obtained by other investigators (Ahrens being neglected). Above the Curie point, i.e. from 626°K. to 640°K. , there are wide deviations, and no satisfactory way of dealing with them is apparent.

In column 9 are given two sets of values for the Curie-point region; the first comprises our own experimental values, column 7, with maximum specific heat at 630°K. ; the second set in brackets, with maximum specific heat at 626°K. , is obtained by weighting Lapp and Grew 1 each, Moser 2, and Sykes and Wilkinson (table 5, column 8) 2. Both sets of figures give the same difference in energy-content from 610°K. to 640°K. to within ± 0.1 per cent.

The range from 400°C. to 600°C. (650°K. to 850°K.). The experimental results available are plotted in figure 4. Although our measurements indicate that impurities have a very small effect on the {specific-heat, temperature} curve in this region, the deviations are very high, amounting to 7 per cent from 400°C. to 450°C. Recently, in an investigation of the {specific-heat, temperature} curve of β brass from 240°C. to 500°C. , Moser's results and our own were in satisfactory agreement, and an independent check was available from a direct energy-content measurement made by Ruer and Kremers: all three experimental methods gave the same result to within ± 0.5 per cent. An error of 7 per cent in either Moser's result or our own at 400°C. to 450°C. is therefore extremely unlikely, and for this reason we have neglected Ahrens's results throughout, as they appear to be consistently high. The

* This transposition does not modify appreciably the values of C_p below 610°K. or above 640°K.

remaining results differ within the reasonable limits of 5 per cent over the region 400° C. to 600° C.

The value of C_p given in column 9 of table 5 at 650° K. is obtained by weighting Lapp and Grew 1 each, Klinkhardt 2, Moser 2, and Sykes and Wilkinson 2. From 700° K. to 800° K. Klinkhardt, Moser, and Sykes and Wilkinson are weighted equally; i.e. each experimental method is considered to be as accurate as any other, in agreement with the arrangement adopted for the most probable {specific-heat, temperature} curve below the Curie point. The value of C_p at 850° K. with this method of weighting is 7.57 cal./gram-atom, which would indicate that Moser's result is in error by 3 per cent.

In the preceding paragraphs we have endeavoured to evaluate the most probable {specific-heat, temperature} curve for nickel on the basis of the existing experimental data. In selecting the data we have been guided by the experimental results given

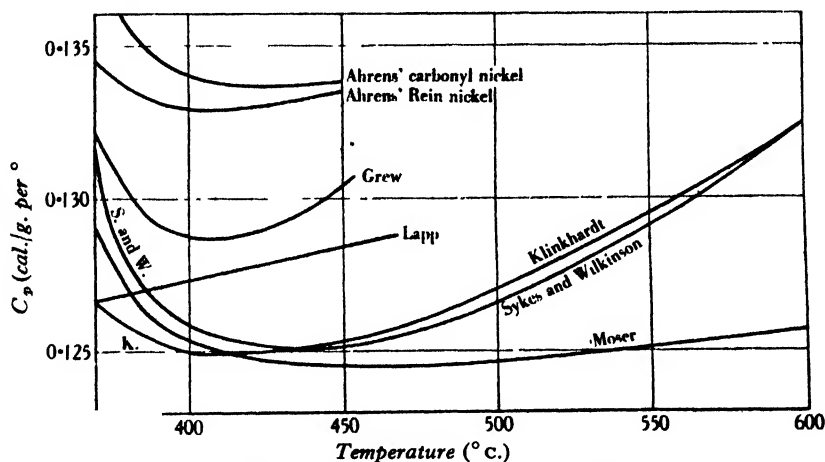


Figure 4. Specific heat from 400° C. to 600° C.

in §§ 4 and 5, which deal with the effects of impurity and the method of preparation of the samples. In weighting the data, each experimental method has been given equal weight because it appeared highly probable that the differences between results obtained by different methods were much more likely to be associated with inherent difficulties in the individual technique employed than with errors in measurement. The values recorded in column 9 should be correct within 0.5 per cent up to the Curie point and 1 per cent above it.

The agreement between our results, column 7, and the most probable values given in column 9 is very satisfactory over the range of temperature 350° K. to 600° K. and 650° K. to 850° K., where direct comparison can be made. In the Curie-point region, 610° K. to 640° K., some uncertainty exists as to the precise form of the {specific-heat, temperature} curve depending on the value chosen for the Curie temperature. The two sets of values given in column 9 are equally satisfactory.

Energy-content measurements. In the region above the Curie point, where the specific heat changes slowly with temperature, measurements by the calorimeter

method should afford a check on those made by the various aneroid methods under discussion. Wust⁽¹²⁾ gives the difference in energy-content of nickel between 400° C. and 600° C. as 25.89 cal./g., the actual value observed by him being 25.56 cal./g. Our value for samples II and III is 25.50 cal./g.

Bronsen⁽¹³⁾, using the calorimeter method and very pure nickel (99.98 per cent), has determined C_p up to 500° C. and finds values of 7.43 cal./gram-atom at 670° K., 7.40 at 720° K. and 7.38 at 770° K., which are in good agreement with those given in columns 7 and 9 of table 5. His value for the Curie point was 358° C. \pm 2° C.

Ewart⁽¹⁴⁾ has recently published measurements which purport to show that a hexagonal modification of nickel exists between 345° C. and 351° C., forming very slowly from the cubic modification on either side. Whilst this work forms the main evidence from specific-heat data for such a modification, it is conceivable that other investigators, including ourselves, did not observe the effect owing to the sluggish character of the transformation from one modification to the other. We doubt whether the accuracy of the calorimeter method is sufficient to justify Ewart's conclusion. From 351° C. to 950° C. the material is cubic, and assuming a linear relation between specific heat and temperature Ewart has evaluated, from energy-content measurements, the values of C_p shown in table 7.

Table 7

Specific heat C_p Temperature (° C.)	0.1267 400	0.1281 500	0.1295 600	0.1310 700
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The difference in energy-content from 400° C. to 600° C. is 25.62 cal./g., a value which should be compared with our mean value of 25.52 cal./g. This agreement is fortuitous, as an examination of the experimental data reveals that the true specific heats, deduced from differences in the energy-content measurements over temperature-intervals of about 100 to 200° C. in this temperature region, actually vary by as much as 10 per cent from those recorded in table 7, whilst the energy-content measurements are liable to an error of \pm 4 per cent.

The evidence from calorimetric data, whilst in good agreement with the results in column 9, table 5, is not sufficiently extensive or precise to give a really satisfactory check.

§ 7. DISCUSSION OF RESULTS

In his theoretical treatment Stoner⁽¹⁾ used the results due to Lapp and Grew over the temperature range 100° K. to 750° K. and Klinkhardt's results from 650° K. upwards. He derives two curves for the variation of C_K , the electronic specific heat, with temperature. One, figure 5(a), is based on the assumption that the electron spins are parallel, and the other, figure 5(b), is the corresponding curve for equal numbers of oppositely directed spins. If the assumption that the observed electronic specific heat at low temperatures, represented by the initial part of figure 5(a), is entirely due to change in the translational state of the electrons is correct, then we should expect that above the Curie point, where there are equal numbers of oppositely directed spins, the electronic specific heat would be represented by the

upper part of figure 5(b). Using Stoner's values for C_Q and $(C_p - C_v)$, we find the values shown in table 8 for C_E above the Curie point:

Table 8

Temperature (° K.)	650	700	750	800	850
Electronic specific heat C_E	1.30	1.11	1.09	1.13	1.22

These fall on the curve for parallel spins, and an error of 3 per cent in C_p would be necessary to lift them on to the other curve. As an error of this magnitude is unlikely, the relation, figure 5(a), between C_E and temperature for parallel spins seems the more probable. The electronic specific heat above the Curie point cannot correspond to parallel spins, and the fact that the observed points fall closely on

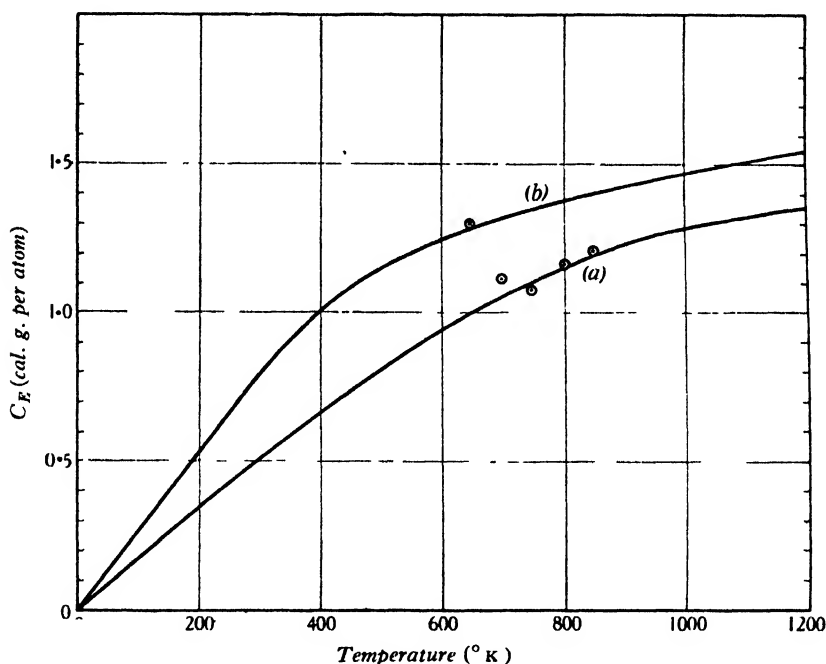


Figure 5

figure 5(a) in this region appears to indicate either that there was an over-simplification in the assumptions underlying the derivation of the curves or that there are other additional factors which have to be taken into account. Whatever the explanation for this anomaly, it seems appropriate to use figure 5(a) for extrapolation to temperatures below the Curie point since it gives the best fit above this point.

The values of C_M are determined by subtracting from C_p the dilatation term $(C_p - C_v)$, the lattice-vibration term C_Q , and the electronic-specific-heat term C_E . As Stoner overestimated C_E his resulting values for C_M are too small. We have redetermined C_M for the temperature interval 450° K. to 630° K., using the data

given by Stoner for C_Q and $(C_p - C_v)$, while the values of C_E were read off from the curve figure 5(a). The resulting values of C_M are as shown in table 9.

Table 9

Temperature (° K.)	450	500	550	600	610	620	622	624	626	628	630
C_p	7.07	7.47	7.83	8.37	8.40	8.69	8.74	8.80	8.89	9.02	9.28
C_Q	5.72	5.77	5.80	5.83	5.83	5.84	5.84	5.84	5.84	5.84	5.84
$C_p - C_v$	0.22	0.26	0.30	0.36	0.37	0.38	0.38	0.39	0.39	0.40	0.40
C_E	0.74	0.81	0.88	0.94	0.95	0.96	0.96	0.97	0.97	0.97	0.97
C_M	0.39	0.63	0.85	1.24	1.34	1.51	1.56	1.60	1.69	1.81	2.07
$\frac{1}{2}(\partial\sigma_0^2/\partial T)$	3.3	4.2	5.8	8.7	9.5	10.4	10.7	11.1	11.8	12.6	13.3
$N\rho$ (c.g.s.u. $\times 10^5$)	0.84	1.07	1.05	1.00	1.00	1.03	1.04	1.03	1.02	1.02	1.11

The molecular field coefficient may be calculated from the following equation:

$$N\rho = C_M \cdot J / \frac{1}{2} \frac{\partial\sigma_0^2}{\partial T} \cdot A,$$

where N is the molecular field, ρ the density, σ the intrinsic magnetization, A the atomic weight of nickel, and J the mechanical equivalent of heat. Values of $\frac{1}{2}(\partial\sigma_0^2/\partial T)$ have been compiled by Stoner⁽¹⁵⁾ from the Weiss-Forrier data for a small nickel specimen with a Curie point at 352°. In the above derivation of C_M the values of $(C_p - C_v)$ are taken from those given by Stoner⁽¹⁾ and slightly transposed to bring the maximum to our measured Curie point of 630° K., and to arrive at $N\rho$ we have similarly transposed the Weiss-Forrier data. The resulting values of $N\rho$ from 500° K. up to the Curie point are practically constant at 1.04×10^5 . This value is about 10 per cent higher than that obtained by Stoner for the Curie-point region.*

At and below the temperature of 600° K. the values of $N\rho$ listed above are much larger than those determined from measurements on magnetization and the magnetocaloric effect, which give $N\rho = 5.5$ to 5.0×10^4 at 600° K. That these low values are incompatible with earlier specific-heat results and with general theoretical considerations has already been pointed out by Stoner, and a possible explanation has been put forward. The present results confirm the view that the discrepancy is not due to errors in specific-heat measurements. Assuming that the value of C_p at 600° K. is in error by 1 per cent, i.e. that the true value is 8.29 cal./g., we find that $C_Q + (C_p - C_v)$ is 6.19 cal./g., leaving 2.10 cal./g. for $C_E + C_M$. If C_M is 0.62 cal./g., the value necessary to make $N\rho$ equal to 5×10^4 , then $C_E = 1.48$ cal./g., which is 0.38 cal./g. higher than the value of C_E at 700° K. and corresponds to an error of 4 per cent in the measured value of C_p at this temperature.

* Dr Stoner has informed us "that further consideration of the problem has shown that the character of the variation of C_E below the Curie point is much more complex than was previously supposed. Detailed calculations are not completed, but the indications are that the values of $N\rho$ calculated by the present method can be regarded only as lower limits to the molecular field coefficient."

§ 8. ACKNOWLEDGEMENTS

The authors are indebted to the Department of Scientific and Industrial Research for the grant made to one of them (H. W.); to the Metropolitan-Vickers Electrical Co. Ltd. for kindly providing the necessary facilities, and to Dr A. P. M. Fleming, C.B.E., Director and Manager of Research and Education Departments, for his personal interest in the investigation. The authors thank Professor W. L. Bragg, F.R.S., and Dr E. C. Stoner, F.R.S., for their kindness in discussing the subject-matter of the paper from time to time.

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THE CONSTRUCTION OF MOLECULAR MODELS OF DIELECTRICS

Demonstration given on 8 April 1938

By L. HARTSHORN, D.Sc.

IN an investigation of the dielectric properties of some synthetic resins the need was felt for models which would give a general idea of the molecular structure of materials of this type; that is to say, of organic compounds with large molecules, which are formed by the linking together of simple molecules by polymerization or condensation. A typical example is the phenol-formaldehyde resin familiar to most physicists as Bakelite. This is commonly used in two forms, one which is fusible and readily soluble in such common solvents as acetone and alcohol and is used for making varnishes, and another which is insoluble and almost vitreous in character and is used in the form of insulating sheets, rods, tubes and mouldings.

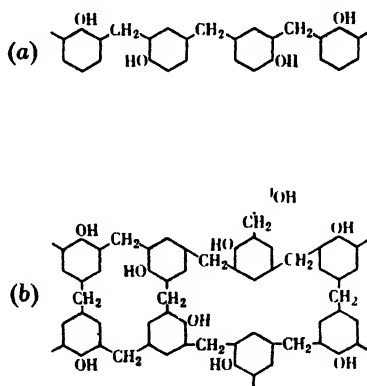


Figure 1. Structure of phenol-formaldehyde resins (a) fusible; (b) heat-hardened.

It is believed from chemical evidence that the structure is more or less such as may be represented by the formulae shown in figure 1. In each case we have benzene rings with hydroxyl groups attached, arising from the phenol molecules, linked together by methylene groups, $\text{—CH}_2\text{—}$ from the formaldehyde molecules. The structure of the fusible resin is fairly easily visualized: it is that of a simple chain. The structure of the hardened resin is, however, difficult to visualize. It may be regarded as a kind of irregular lattice-structure obtained by cross-linking a number of neighbouring chains. The structure lacks the regularity of a crystal, and it is evident that the ordinary graphical formula can give very little idea of the spatial relations between its constituent atoms and groups. I have found a model constructed with wooden balls to represent the various atoms very informative in this respect.

When the need for these models first arose, I naturally turned to the well-known work of Sir William Bragg and the workers at the Royal Institution, and also the models of proteins recently shown to the Physical Society by Dr Winch. I soon found that the construction of models may absorb a good deal of time and money, and having now arrived at a relatively cheap and simple method of construction, I propose to describe it in the hope that it may be useful to those who have similar problems. It will be found that with a stock of a few kinds of wooden balls of the type to be described, a model of the molecule of almost any organic material may be constructed in a few minutes, and although it will have no pretensions to accuracy of dimensions, it will bring out features of the structure which are not easily grasped without the use of models.

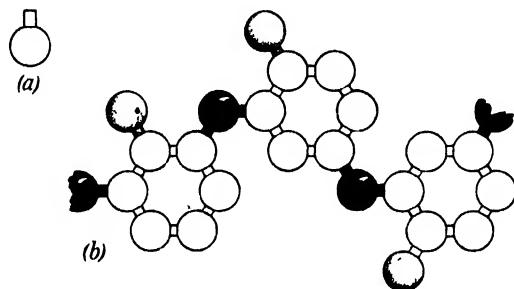


Figure 2. (a) Ball foot as purchased; (b) Model for fusible phenol-formaldehyde resin (Novolak).

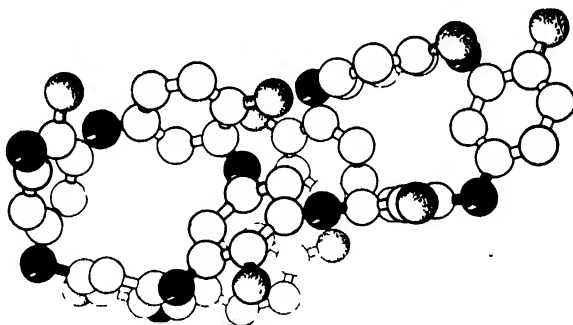


Figure 3. Model for hardened phenol-formaldehyde resin (Bakelite). (Heat-hardened Bakelite.)

The method of construction will be understood by reference to the models for the two phenol-formaldehyde resins already mentioned. That for the fusible resin is shown in figure 2, and that for the hardened resin in figure 3. Both models are built of units of three kinds only, white balls in hexagon formation representing aromatic carbon atoms assembled into benzene rings, black balls linking together the hexagons and representing $\text{—CH}_2\text{—}$ groups, and spotted balls representing OH groups. The hydrogen atoms must be regarded as buried within the carbon and oxygen atoms to which they are attached, since X-ray analysis fails to detect the H atoms as separate units in such compounds as have been analysed. Thus three types of ball are required to represent (1) aromatic carbon atoms for building benzene hexagons, (2) aliphatic carbon atoms each with four bonds symmetrically arranged so

as to occupy the four corners of an imaginary tetrahedron whose centre coincides with that of the ball, and (3) oxygen atoms with two bonds or points of attachment.

These atomic units are all made from "ball feet",* which consist of wooden balls attached to short cylindrical stems, figure 2 (a). They are obtainable very cheaply in three sizes, of diameters $\frac{1}{2}$, $\frac{3}{4}$ and $1\frac{1}{4}$ in. In order to make the hexagons, the balls are placed in a simple jig, figure 4, which consists merely of a board drilled with holes into which the pegs of the ball feet will fit, and mounted at an angle of 60° to the horizontal. The ball is drilled centrally with a vertical drill of the same diameter as the peg of the ball foot. It is then rotated about its peg through 180° and again drilled. Six balls, drilled in this way and arranged so that the stem of one fits into a hole in the next, form a benzene molecule, the hydrogen atoms being represented by the holes which are left empty. The aliphatic carbon atoms are made in

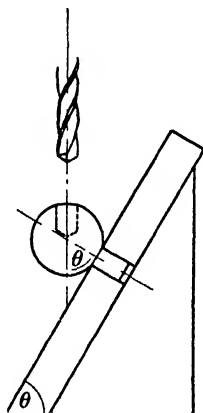


Figure 4. Jig for drilling ball-feet. $\theta = 60^\circ$ for aromatic carbon atoms.
 $\theta = 71^\circ$ for aliphatic carbon atoms.

the same way, but in this case the angle of the jig is 71° instead of 60° , and the ball is rotated about its peg through 120° instead of 180° after each drilling operation, so that each of these balls has three holes and one peg, with their axes inclined to one another at the tetrahedral angle of 109° and therefore representing the four bonds. Additional pegs to fit the holes are cut from dowel rods when required. The balls are very easily coloured by dipping them into black, red, green or yellow ink. The $\frac{3}{4}$ -in. ball is the most convenient one for most purposes. It serves for both carbon and oxygen atoms since X-ray data obtained for organic compounds show that these atoms are of about the same size. The chlorine atom is considerably bigger, and may be represented by the $1\frac{1}{4}$ -in. ball. A slightly smaller size would be more nearly to scale, but no other sizes appear to be produced so cheaply.

It is a simple matter to prepare a stock of a few dozen balls of each of these kinds, and with them molecular models of the kind shown are very quickly assembled. The models shown represent (1) fusible phenol-formaldehyde resin (Novolak).

* Supplied by Messrs Hobbies, Ltd., 16, New Oxford St., London, W.C. 1.

This is a chain structure, assembled as shown in figure 2; (2) hardened phenol-formaldehyde resin (Bakelite), figure 3, a structure of an irregular lattice type. It cannot be claimed that this model represents in detail the actual structure of any one molecule, but it is reasonable to suppose that the benzene rings preserve their usual configuration, and that the possible positions and orientations of the links of the structure are fixed by the geometry of these hexagons and the tetrahedral carbon atoms. Obviously many cross-linked structures differing in their details could be assembled from the same numbers of atoms of the various kinds, and there is at present no means of discriminating between the various possibilities. The

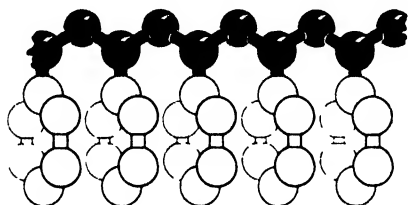


Figure 5. Model for polystyrene.

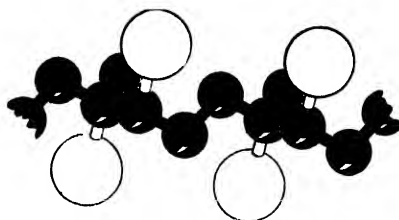


Figure 6. Model for chlorinated rubber.

model does, however, give some idea of the general features of the structure, such as its rigidity, the open spaces, and the distribution of the OH groups, which, being polar, greatly affect the dielectric properties; (3) polystyrene, figure 5. This may be regarded as an aliphatic hydrocarbon chain with benzene rings attached to it. The material is a clear transparent resin with excellent insulating properties. On the scale of the model a complete molecule would be represented by a chain some 30 m. long; (4) chlorinated rubber, figure 6, another chain compound. The large chlorine atoms are easily distinguished.

Models of methyl methacrylate, cellulose acetate, and chlorinated diphenyl also were shown.

I am much indebted to Mr E. J. Pratt for preparing the illustrations. For the sake of clearness a portion of the peg of each ball is shown; in practice the peg is not usually visible after it has been inserted into the appropriate socket in order to link together two balls. The problem of giving an impression of the models by means of photographs or diagrams is one of considerable difficulty, a fact which serves to emphasize the usefulness of the model.

THE DISSIPATION OF ENERGY BY A PENDULUM SWINGING IN AIR

THE AMPLITUDE DEVIATION OF RATE OF A PENDULUM: A SECOND EXPERIMENT

By E. C. ATKINSON, M.A.

See page 756 of this volume

AUTHOR'S REPLY TO DISCUSSION

Do not Dr Rawlings's observations with the gyro wheel show that the viscosity of air increases with the density? I am not sure that the changes in pendulum resistance prove this to be the case, because, in addition to skin-friction loss, energy is dissipated by the movement of the air. Would not this component increase with density even if viscosity remained constant? I cannot answer the question about low pressure loss from my own experience, but I refer Dr Rawlings to Loomis's observations (§ 13) and to Dr R. d'E. Atkinson's remark in this discussion.

My observations show that the loss of energy due to the rubbing friction of the impulse lever on the pendulum rod may be very small. For small amplitudes the relative motion is of the second order only, if a point on the rod does not describe a circle or if the axis of the lever is too high or too low, and in such cases the losses are probably negligible. On the other hand, when the lever axis is in the wrong vertical plane, either displaced to one side of the right one or inclined to it, slip is of the first order and energy loss may be serious.

I cannot answer Dr Kantorowicz's question about yield point. I used brass chaps and I doubt whether the rivets clamped the faces tight enough together to reach the yield point even of the brass. When a spring is made non-uniform by varying the width instead of the thickness the internal loss will be far less, as Dr Kantorowicz suggests. This form has the disadvantage for pendulum suspension of making a less compact spring.

Mr Hope Jones makes the calculation of input of energy appear simpler than it really is, for part of the energy released by the fall of the lever remains with it as kinetic energy. Using data about the Synchronome lever which Mr Hope Jones gave me 10 years ago, I conclude that of 94 ergs released about 71 are transferred to the pendulum when the amplitude is 50' and 68 when it is 60'.

I do not use the Synchronome remontoire, but I replace the gravity lever with an electromagnet just as Mr Cottingham did, except that I use a thermionic valve in such a way that contact between pendulum and impulse lever lowers the grid voltage and so cuts off the anode current which energizes the electromagnet. With suitable screens attached to pendulum and armature lever this voltage change can be made by means of a photoelectric cell but I doubt whether this method is as reliable as the simpler one.

As variation of the arc of the impulse, to which Mr Hope Jones refers, is the worst fault of the gravity impulse, it is important to guard against it. When the armature lever comes fully into contact with the clean ends of the stop screws the arc is very nearly constant. In order to test whether all is well, I switch on a telephone circuit which is completed by contact between lever and screw. The sound at make shows whether the contact is clean and whether there is recoil.

The Foucault effect produces twist in the suspension spring and so affects its rigidity for the normal motion. Has Mr Cottingham managed to calculate the moment necessary to counter the effect? Lack of symmetry in the pendulum produces an alternating twist in the spring and I suspect that this is likely to be more harmful than the Foucault effect.

It is interesting that Mr Cottingham used Newton's rings so long ago to observe the motion of a pendulum support. If one could measure the motion in this way and also measure the loss of energy due to motion through a cycle of known amplitude, it would be possible to separate the spring loss from the bracketing loss, as Mr Hope Jones desires.

Dr Atkinson's observations on decrement with clamped and with all-one-piece quartz fibres are very interesting. I do not know whether a spring can be ground so as to secure cycloidal motion of the bob, for I have not dealt with the second-approximation terms of the equations of motion. I think Haag alone has attempted to obtain these terms. If Dr Atkinson will read Haag's paper, he will perhaps be able to clear up some of my difficulties and doubts.

REVIEWS OF BOOKS

Isaac Newton 1642-1727, by J. W. N. SULLIVAN, with a memoir of the author by CHARLES SINGER. Pp. xx + 275. (Macmillan & Co., Ltd.) 8s. 6d. nett.

This book, over which Sullivan spent considerable time during his last ten years, presents a very interesting but unusual account of Newton's life and work. Most readers of Newton's biography will have noticed how in several respects his behaviour differed very much from what one would normally expect of a discoverer. Thus he put on one side his work on gravitation, when it had reached a most interesting stage in 1666, although he then "minded mathematics and philosophy more than at any time since". A portion of his book on optics published in 1704 was "written at the desire of some Gentlemen of the Royal Society, in the Year 1675... and the rest was added about twelve Years after to complete the Theory." He goes on to say "to avoid being engaged in Disputes about these Matters, I have hitherto delayed the printing, and should still have delayed it, had not the importunity of Friends prevailed upon me." Most of his scientific work was accomplished by the time he was forty-five, when, in one tremendous effort lasting eighteen months, he composed the *Principia*; but it might never have been written had it not been for an almost accidental discussion with Halley and "the importunity of friends". He was apparently indifferent to the claims of others, such as Hooke, and in connexion with Leibnitz his case was at first argued by his friends.

Sullivan aims at explaining these unusual characteristics and suggests as the solution of the problem that Newton was not interested in philosophy and did not regard even his greatest discoveries as being of importance. It is surprising to find it suggested that our greatest mathematical physicist was not really interested in science and that he only worked when, for accidental reasons, the spirit moved him. Nevertheless the explanation seems to fit the facts in many instances.

Thus when he "compared the force required to keep the moon in her orb with the force of gravity at the surface of the earth and found them answer pretty well", that ended the matter. Various hypotheses have been advanced to explain this. Pemberton suggested that he used an incorrect value for the length of a degree of latitude, but it is known that he had access to a reasonably correct one. Adams and Glaisher suggested that it was not until 1685, when Newton proved that a sphere attracted as if its mass were concentrated at its centre, that he felt that the law of gravitation was established. This proof made exact what he formerly regarded as approximate, much to his own surprise. Be that as it may, Newton in 1666 was personally satisfied "pretty well".

To Sullivan this dropping of the subject indicates his lack of interest. He was more interested in alchemy and in religion, and apparently regarded it as more important "to justify the ways of God to man" than to explain the motions of the heavens.

Similarly in connexion with the claims of Hooke and of Leibnitz, he ignores them until they seem to affect his personal honour. He is then aroused and writes severely to Hooke and superintends the preparation of the second edition of the *Commercium Epistolicum*. He is aroused from his duties at the Mint and his religious studies by the problems of Bernoulli, which he solves in a night, since he feels they are a challenge and attack on his method of fluxions. He is aroused for a moment only.

Thus we have a picture of Newton indifferent to science and perhaps, like Pascal, half ashamed of spending his time in mathematics, and like Cavendish not interested in publication of his work. Sullivan presents his arguments most convincingly and they are supported by lengthy and pertinent extracts from Newton's letters and those of his contemporaries. These apart from Sullivan's thesis are interesting side-lights on a very

interesting period of English science. It is, of course, impossible to say whether Sullivan's explanation is correct. It seems to explain much, but it does not explain Newton's most regular attendances at the meetings of the Royal Society over which he presided from 1703 until 1727, when, though in a poor state of health, he presided for the last time three weeks before his death.

H. B.

Probleme der Technischen Magnetisierungskurve. Herausgegeben von R. BECKER, Göttingen. Pp. v+172, with 102 illustrations. (Berlin. Springer, 1938.) RM: 16.50.

The contents of this book consist of the contributions made at a colloquium held in Göttingen in October 1937, to discuss ferromagnetic problems of technical importance, and they are of interest to all who are concerned with such problems. It may be said at the outset that many of the speakers appeared to attach great significance to the properties of boundaries between magnetic domains. Thus, the first contribution by K. J. Sixtus on the researches carried out on the propagation of large Barkhausen discontinuities and their theoretical interpretation is followed by another in which W. Döring examines the energy relations in the transition region of separation between two oppositely magnetized portions of a wire which represents a discontinuity spreading along the latter. On account of its technical interest, coercivity loomed large in the discussions. M. Kersten in his contribution reviews the modern conceptions of coercive force, and he also placed emphasis on the information which the investigation of large Barkhausen discontinuities has provided and upon the conception of a wall or transition region between adjacent domains magnetized anti-parallel to one another.

The reviewer found the sections on magnetic viscosity to be the most interesting. This subject has been more or less completely ignored in modern works, mainly because the observed effects are generally quite small. G. Richter, however, gives an abbreviated account of his magnetometer and ballistic studies of the pronounced effects exhibited by carbonyl iron, which shows marked induction changes up to 100 seconds after the magnetizing field has become steady. Richter shows that magnetic viscosity and ordinary hysteresis effects are not intimately related. His main results are confirmed by H. Schulze, who gives a summary of the results of an alternating-current study of the phenomena which was recently published by the Siemens-Werken. He measures the power losses in a carbonyl iron core by means of a Maxwell inductance-capacity bridge and separates them into magnetic viscosity, hysteresis and eddy-current losses. He shows that the viscosity losses can be divided into two parts, one independent of and the other dependent upon the frequency of the alternating field. The latter part provides a kind of resonance curve when plotted as a function of the temperature of the specimen for a constant frequency f , the relation between f and the absolute temperature T_r at which the viscosity is a maximum being given by

$$\log 2\pi f = \theta \left(\frac{1}{T_0} - \frac{1}{T_r} \right) = 34.7 - \frac{10,600}{T_r}$$

for the material in the virgin state. Schulze explains his results on the assumption that a pure and recrystallized specimen of carbonyl iron in the virgin state consists of parallel, threadlike domains magnetized in parallel and antiparallel directions.

The final contributions describe new ways and apparatus for applying magnetic analysis to problems of metallic structure. Here the reviewer is not happy about some of the basic assumptions and interpretations. In particular, he deprecates the use of the term "spezifische technische Sättigung $I_{\infty, T}$ " to denote what he would himself describe as the "spontaneous magnetization in zero applied field $I_{0, T}$ " at a temperature T . However, the book is full of interest and is to be heartily commended.

L. F. B.

Negative Ions, by H. S. W. MASSEY. Cambridge Physical Tracts. Pp. xiv + 105. (Cambridge University Press.) 6s. net.

This work is the first of a series of Cambridge Physical Tracts issued under the joint editorship of Professor Oliphant and Mr Ratcliffe. It is the aim of the editors that these tracts may present such surveys of subjects as the authors might give in a short course of specialized lectures. They are therefore intended not to be exhaustive but to deal more particularly with work on which the authors can speak with direct experience gained through their own investigations. Such a tract avoids one objection to a full monograph, complete with all references to published papers and to allied subjects which, in a rapidly advancing subject, becomes so soon out of date. In these tracts, bound in a stiff paper cover and issued at a moderate price, revision or additions in subsequent years will be much more practicable, and it is to be hoped that other authors will come forward to supply a real need in the busy life of the average physicist.

The material collected by Dr Massey in a hundred pages is full of interest and is well selected. The first two chapters summarize the experimental evidence for the existence of certain atomic and molecular negative ions in gases, and discuss from the wave-mechanical standpoint why one would expect stable ions in certain cases and not in others. The third chapter, on modes of formation, is of particular interest and deals with the processes of electron-capture and the experiments of Tate and Lozier, Bailey, and Bradbury. In the last chapter, on negative ions in glow discharges and the upper atmosphere, the author draws attention to a number of problems which still await solution, and makes tentative suggestions as to the role played by negative ions in the conducting layers of the ionosphere.

The tract may be confidently recommended as a critical and original treatment of a subject which has not previously been adequately summarized. A. M. T.

Direct and Alternating Current Potentiometer Measurements, by D. C. GALL, F.Inst.P. Pp. xiv + 231. (Chapman & Hall.) 15s.

This book constitutes volume IV of the series of *Monographs on Electrical Engineering* edited by Mr H. P. Young. The author is well known as a designer of electrical instruments, and has himself originated instruments of the classes which form the subject of the volume.

The direct-current potentiometer has long been a familiar instrument both to physicist and engineer. Its accuracy and the multiplicity of its uses, direct and indirect, are well recognized. The alternating-current potentiometer is its younger brother, a decidedly subtler and more complicated personality. In 1897 Clark Fisher produced his book on *The Potentiometer and its Adjuncts*; in this the alternating-current instrument is not even mentioned, although the idea of it had already begun to take practical form. The first complete alternating-current potentiometer, that of Drysdale, appeared in 1908. Its reception was not at first general, and even as late as 1922, in the *Dictionary of Applied Physics*, we find the alternating-current potentiometer disposed of in three quarters of a page, whilst the direct-current instrument claims fourteen pages.

The book before us is, we believe, the first since Fisher's to be devoted entirely to the subject of potentiometers; about one quarter of it (five chapters) is allotted to the direct-current class, and three quarters (eight chapters) to the alternating-current class of instrument. Doubtless this proportion is not intended to indicate the relative order of importance, but rather to implement the view that the time is ripe for a full-dress introduction of the manifold applications and merits of the new-comer. We feel sure the book will be sincerely welcomed by the physicist as well as the engineer. The description of the various forms of instruments of the direct-current and alternating-current types is given with the wealth of practical detail and suggestion that would be expected from the author, and the notes and bibliography appended to most of the chapters facilitate access to the whole field of potentiometer measurements.

Of the chapters on the direct-current instruments no more need be said than that fresh material will be found even for the expert. The reader's attention is however directed mainly to the alternating-current types of potentiometers. Two chapters are devoted to descriptions of the instruments, and four chapters to their applications, which range from the calibration of ammeters, voltmeters and watt-meters to measurements of impedance of all kinds, the determination of iron losses, the testing of current and potential transformers, and the measurement of magnetic fields. The author has developed the rectangular-coordinate type of alternating-current potentiometer, and the interest of the reader will naturally turn to his account of his own instrument. It will be found that the balance is held fairly between the polar and the coordinate types, applications to which one or the other type is peculiarly adapted being pointed out. One valuable chapter is devoted to the precautions to be attended to when the most precise measurements are required. In a penultimate chapter the representation of alternating-currents or voltages by complex quantities is explained in its application to the calculation of results from measurements made with the coordinate type and with the polar type of potentiometer respectively. A brief historical chapter brings the book to its close.

If a criticism may be made it is that more care might occasionally have been allowed in the exposition of theory and the unambiguous choice of symbols. The manipulation of alternating-current quantities undoubtedly presents difficulties to the learner, and in view of the necessity of distinguishing clearly between instantaneous value, amplitude, effective value, and vector value, special regard to a systematic notation and nomenclature is demanded. This impression should not impede for a moment the recourse of any reader interested in electrical measurements to the benefits to be derived from this valuable and timely book.

D. O.

Elementary Practical Physics, by N. H. BLACK and H. N. DAVIS. Pp. viii + 710. (New York: The Macmillan Co., 1938.) 8s. 6d. net.

This is not, as many English readers might expect it to be, an elementary laboratory manual. It is mainly devoted to what we might call, for want of a better brief title, "Everyday Physics", or since the cyclotron, which gets over two pages of description, is not yet an everyday object even of the laboratory, perhaps "Elementary Applied Physics" would be a less misleading title.

The book does deal very largely with the physics of everyday life—the motor-car provides the first object-lesson—and the authors (a Harvard physicist and a former Harvard engineer) form an obviously suitable team for the writing of such a treatise. One of their avowed aims is the teaching of physics "in the light of its social and industrial uses", and this aim is followed throughout the book. Considerable space is, however, given to quite recent developments, of which the "practical" applications lie largely in the future.

The text is brightly written, and is supplemented by a large number of diagrams and an excellent selection of most searching questions, so worded as to catch the attention and linger in the memory—e.g., "Does the cardboard jacket on a dry cell serve any useful purpose except advertising?" The questions range far outside the subject-matter of the text, and the reader is enjoined to consult reference books in attempting to answer them, "to keep his eyes open outside the classroom and to ask questions of artisans and businessmen". This seems on the face of it excellent advice, and it is difficult to believe that it can be the same authors who on another page (299) advocate the starting of a first-class squabble thus: "Will potatoes cook faster if more gas is turned on to make the water boil faster? *Discuss it with your mother.*" The authors again show, we feel, less than their usual acumen when they encourage the young reader to float silver coins on mercury—the success of this experiment may very well be accepted as an act of faith.

The book is further embellished by portraits of outstanding physicists, intelligently arranged. Thus, Joule is paired with Kelvin on one page, and Henry with Faraday on another. The authors have succeeded in securing a rather rare photograph of Moseley, which they have fittingly placed with Rutherford's, and Marconi's portrait is associated with that of Hertz—we may hope that a place will be found for Maxwell in the next edition. The portraits—of which there are many others—add considerably to the interest of the book.

Any intelligent youngster could learn a good deal of interesting physics from this volume, and a senior who had studied it carefully might be less apt to leap like a startled faun at the well-known gambit: "Look here, you're a physicist, you can tell me why. . ."

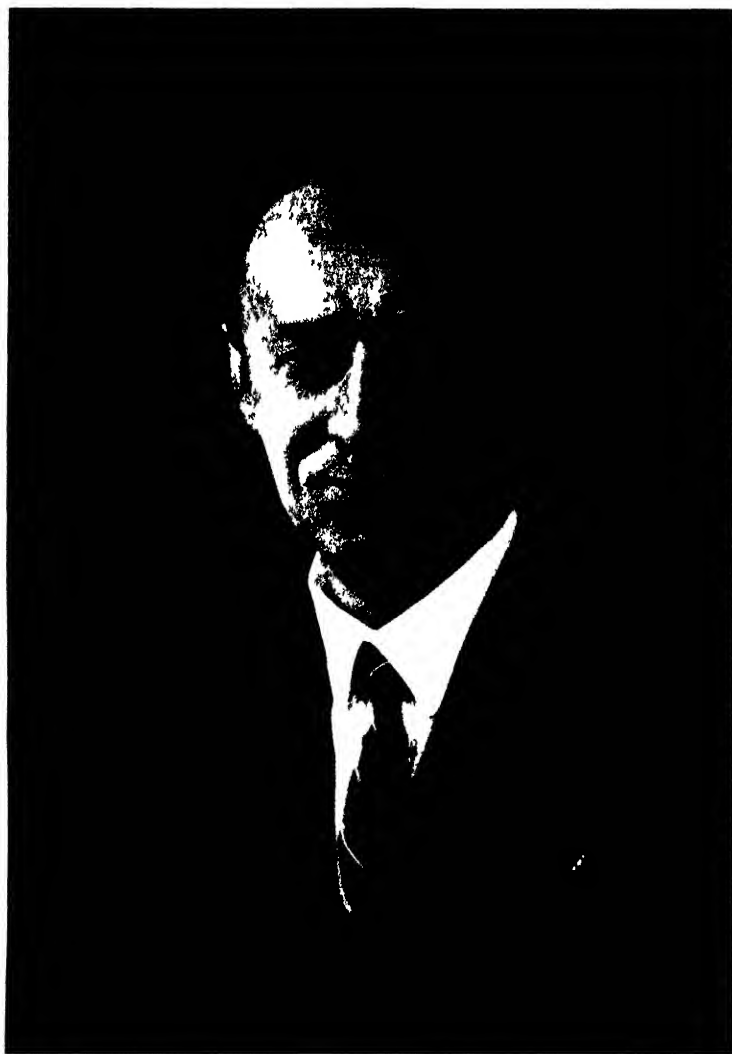
The book is an experiment, interesting and on the whole very successful. In view of its size and the lavish way in which it is illustrated, the price is remarkably low. H. R. R.

On Understanding Physics, by W. H. WATSON, M.A., Ph.D., F.R.S.C. Pp. xii + 146. (Cambridge University Press.) 7s. 6d.

Prof. Watson, who is Assistant Professor of Physics in McGill University, has evidently been troubled, like many other experimental physicists, by the repercussions of so-called modern physics on philosophy. He is particularly concerned with the philosophers' writings around the discoveries made by experiment. This book contains his reflections, which are based largely on the views of Dr Ludwig Wittgenstein. The problems are treated from the standpoint of the logician rather than from that of the mathematical physicist, though "language is, of course, a more complicated symbolism than mathematics". The chapter on "Methods of Representation" is particularly good and should be read with equal interest by both experimental and theoretical physicists. On the controversial question of determinism the author says "... the new theories of physics will not do for us what not a few men have wanted them to do, namely, to get rid of determinism" (p. 80). And on discontinuity he says "if it happens that discontinuity is accepted, and with it limits on the precision with which an electromagnetic field can be specified, perhaps we shall be fortunate enough to avoid the mistake of attempting to use the new physical theory as a peg on which to hang 'philosophy'" (p. 141).

Although the book makes difficult reading, which is inherent in its nature, it is one of those which serves to give scientists in general and physicists in particular a view of the recent outstanding advances in physics, in relation to the background of philosophical thought; it also serves to restrain the making of broad generalizations from theories propounded for the purpose of linking together, in logical order, discoveries made by experimentalists.

H. R. L.



THOMAS SMITH, M.A., F.Inst.P., F.R.S.
President of the Physical Society, 1936 to 1938

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VISION THROUGH OPTICAL INSTRUMENTS

By T. SMITH, F.R.S.

Presidential address delivered on 25 February 1938

IN recent years I think no President has chosen an optical subject on which to address the Society. This is certainly the case since the Physical Society, as we know it now, came into being through the amalgamation of the Physical Society of London and the Optical Society. It is not therefore inappropriate that I should begin by referring to the position in our Society of optics as a part of physics in which many of our Fellows are especially interested.

At first after the amalgamation all optical papers were read at one of the ordinary meetings. When these times proved less convenient, for those more particularly interested, than those of the Optical Society's meetings had been, special meetings were arranged with all-optical programmes. From the first these meetings have been successful, but as they are conditioned by the supply of suitable papers their frequency is uncertain, and it has not been possible to arrange them as long in advance as the other meetings. For various reasons it has seemed desirable to read certain optical papers at the ordinary Friday afternoon meetings; but the special meetings for the reading of most of the optical communications will be continued if this course commends itself to the Society.

These special meetings are perhaps the beginnings of a process which may well extend. The number of papers accepted for publication is such that many have to be read only in title, and among these there may be some which in other circumstances would provoke discussions of particular value to workers in special subjects. I see no reason why groups of Fellows with special interests should not be able from time to time to arrange additional meetings, at times convenient to themselves, for reading papers or holding discussions: nor need it be assumed that London is the place for them. Sooner or later I think we shall have a number of sections holding their own meetings in addition to the general meetings. Moreover, the formation of local branches in suitable centres might well add to the value of the Society to Fellows living at a distance from London; and if this came to pass I hope a number of papers accepted by the Council for publication in the Proceedings would be made available for reading at these centres. The provincial meetings held hitherto have been most enjoyable and successful, and I think the experience of Institutions such

as the Electrical Engineers should encourage the Council to allow the Society to expand along similar lines. I ought to add that in saying this I am only expressing my personal views, for no proposal of the kind is or has been before the Council. But I am confident that the Council will always be ready to take whatever action promises to be most effective for the advancement of physics and the diffusion of physical knowledge in this country.

Reverting however to optics, I would remind you that among the special publications of the Physical Society in recent years are two closely connected with the subject I have chosen to speak on to-night—those dealing with the teaching of Geometrical Optics, more particularly in the elementary stage. The second of these, prepared by a Committee on which several experienced teachers served, contains unanimous recommendations on the signs to be given to fundamental magnitudes, and further proposes that the choice of a sign convention for other quantities should be restricted to two systems, which are constructed on different principles. It was recognized that the recommendations would involve schools generally in no little difficulty, for the current text books almost without exception used conventions opposed to some of those recommended. Despite this obstacle, the importance of aligning teaching with technical practice has been widely recognized, and I understand that the recommendations of the report, where they are unanimous, are being more and more extensively followed. There is every reason to expect that before long they will be adopted in all schools and colleges in this country. The publication of the report, and of the papers and discussion which preceded it, has indubitably contributed materially to the advancement of optical knowledge.

It is less easy to speak about the effect of those recommendations where alternatives were proposed. Inevitably a considerable time must elapse before a general preference for one convention rather than another becomes manifest. It will be remembered that one system makes use of a cartesian framework fitted to the optical system. There has been no dearth of technical books using this system, and these have no doubt been useful for constructing elementary courses in which this set of conventions is applied systematically. This system has also the advantage of being familiar in other fields. The alternative proposed by the Committee may be described as the “real-is-positive” system. The absence of school text books using this system has probably proved an initial handicap, but I expect (for I have had no opportunity of investigating it) that this is no longer the case. From personal correspondence I know that this set of conventions appeals strongly to some teachers, and I was recently told by a teaching member of the Committee that indications of a preference for this system among Science masters are not lacking. The efforts they are making to present this, as well as other parts of physics, in ways which appeal to the average boy or girl, will be watched with sympathy and interest by us all. That the tendency is towards the real-is-positive convention is also the conclusion Prof. H. S. Allen (space-systems is his description of the class to which it belongs) reaches in a review of several new optical texts. It is interesting to find that there is a real desire among school and university teachers to achieve the general adoption of a single convention. The weight they attach to uniformity is

important because it is in the elementary work that these conventions matter. They are less important in more advanced work, not so much because the more experienced student can be expected to adapt himself readily to any conventions, as because conventions hardly enter into the later stages of the subject.

Technical instruction in ophthalmic optics was not discussed in the report. The foundations of the curvature method now in such general use were laid and built upon by a succession of able teachers armed with an intimate knowledge of conditions in the spectacle industry; hence no changes of convention have been required. The curvature method has the virtue of making pupils realize that the course taken by light is determined by the properties of a finite volume, not those of a vanishingly thin filament, of the media it traverses. For the present-day needs of the spectacle industry this system of optics seems to be well suited; in schools it can with advantage be kept in reserve as an alternative method of developing the theory, and I understand that when time permits it is found valuable in revision courses. But, notwithstanding its undeniable merits, the curvature method appears to me to possess difficulties, and perhaps limitations, of its own, which to some extent arise from the very features which have proved its outstanding virtues. Curiously enough it is in visual problems and in dealing with systems which do not possess rotational symmetry, the very conditions in which it is applied more extensively than any other system, that these difficulties arise.

Using the notation of the two systems that I have referred to—the real-is-positive and the curvature system—I think it will hardly be disputed that the treatment is made to rest on the two equations

$$\frac{1}{u} + \frac{1}{v} = \frac{1}{f} \quad \text{or} \quad L' = L + F$$

and $\text{magnification} = -\frac{v}{u} \quad \text{or} \quad \text{magnification} = \frac{L}{L'}.$

The ideas of focal length or power, and of magnification, are assumed to be adequate for the discussion of all questions that may arise. I have no reason to suppose that in this respect the newer books differ substantially from their predecessors. It is quite possible on these foundations to give a theory adequate for what I call Laboratory Optics. For instance we can deal with the sizes and positions of images, and devise lens systems for photography or for recording with such instruments as thermopiles and photoelectric cells. But when we consider visual instruments all this seems rather inappropriate. We cannot readily measure the overall magnification for a system including the eye, and it is not clear that we are seriously concerned with the power of such a combination. Our interest should surely lie in the properties of the instrument as they affect the appearance of the picture presented to us; in this respect the treatment now followed seems to me unquestionably defective. Indeed we might well wonder whether the writers of modern books have ever looked through a lens or other optical instrument, except to search for pins. Nor is the omission confined to elementary books. I have recently made an extensive examination of many modern works dealing with the more advanced parts of optics.

In only one of these have I found any mention of part of the general theory which I think is of great importance; and even there it is treated so lightly as to suggest that its significance has not been properly appreciated. I wish in this address to point out where I think the current theory needs augmenting, and to indicate some difficulties which those who adopt the curvature system for all purposes should consider. Perhaps it will be as well for me to say at once that in this discussion nothing difficult or abstruse is involved.

Now it is very easy when we are constructing a scientific theory to overlook facts that are familiar to us. The simpler and more obvious the fact the more likely it is to remain below that level of consciousness at which we recognize it as a fact that demands attention. We are going to consider whether we have not formed a habit of overlooking something which we know, but disregard because it is so familiar. On such a quest it may not be unwise to start in the nursery.

I expect most of us still have some recollection of Hans Andersen's tales. The one I would recall now would doubtless be classed by *The Times* under A rather than U, both because it is highly immoral, and because so many morals can be drawn from it. In *The Tinder Box* we read of a soldier meeting a witch as he was on his way home from the wars. This is what the witch tells the soldier:

"When you reach the bottom of the tree, you will find yourself in a large hall: it is quite light, for there are more than a hundred lamps. Then you will see three doors which you can open, for the keys are in the locks. If you go into the first room, you will see, in the middle of the floor, a large box on which a dog sits; it has eyes as big as tea-cups, but you need not mind it. I will give you my blue check apron, which you must spread out upon the floor, then walk straight to the dog, lay hold of it, and set it upon my apron, open the box and take as many pennies as you like. It is all copper money; but if you would rather have silver you must go into the next room. There sits a dog with eyes as large as the wheels of a water-mill, but do not mind that; set it upon my apron and take the money. If however you want gold, you can have that too, and as much of it as you like to carry, by going into the third room. But the dog that sits on the money-box has two eyes, each one as big as the Round Tower of Copenhagen. That is a dog, I can tell you! But never mind him, only put him upon my apron, when he will not hurt you, and take as much gold out of the box as you like!"

Now I suppose we should all share to some extent in the emotion the witch mentions if we suddenly met dogs of this breed. But it is the dogs themselves, or rather the character of their vision, that I want to consider. What would a man appear like to a dog with eyes as big as tea cups? I suppose the soldier expected to be regarded as an insignificant being, if not indeed small and obnoxious enough to be a natural prey. But a reflecting man might have thought, "the curvature of this dog's eyes must be relatively small, and the focal length therefore long; so I shall appear larger to him than I should to an ordinary dog. He will probably be intimidated by my apparent bigness, so I need not fear him." Now whether this argument is correct, or whether it was the blue check apron that kept the dog subdued, the story does not tell us. The witch may have known, but as the soldier

cut off her head, her knowledge is not available for us. The soldier himself doubtless cared nothing for these things.

That is one way of introducing the subject. I think I might fairly call it the physicist's way. There is another, the mathematician's. This might run:

"When we are dealing with a pair of conjugate points the quantity

$$\frac{1}{f} - \frac{1}{u} - \frac{1}{v} \quad \text{or} \quad F + L - L'$$

vanishes. What is the meaning of this quantity when the points are not conjugate?"

Of course it requires unusual perspicacity to recognize one question as a translation of the other. To be honest I must admit that they are not exactly equivalent. The equations are not in fact written in their physically most significant form; as they appear at the moment we cannot give a sensible physical meaning to the quantity we are asked to consider.

It will be simpler for us to return to the physicist. Failing the dogs, we make our own eyes bigger by putting a telescope or binoculars in front of them. The kind of thing we then see is no doubt familiar to us all, and noticeable in many newspaper illustrations. A very obvious feature is the way in which distances close up. The newspaper from which my lantern slides have been prepared does not publish pictures in which this effect is very pronounced, but I dare say that many of you can recall seeing extreme examples in some of the evening papers; for instance in a cricket picture the bowler may appear right on the top of the batsman at the other wicket, and the pitch seem only two or three yards long. This effect is familiar to everyone who uses binoculars, and of course an explanation can be offered starting from the usual equations. The line of reasoning generally accepted is, I think, on these lines:

If we have two pairs of conjugate points 1 and 2, from the two equations

$$\frac{1}{u_1} + \frac{1}{v_1} = \frac{1}{f} \quad \text{and} \quad \frac{1}{u_2} + \frac{1}{v_2} = \frac{1}{f}$$

we obtain by subtraction a relation which can be written

$$\frac{v_1 \sim v_2}{u_1 \sim u_2} = \frac{v_1 v_2}{u_1 u_2}.$$

This is expressed in the doctrine that the longitudinal magnification is the square of the lateral magnification. It is simple to show that this is true in any instrument having rotational symmetry. The argument then runs that the instrument forms diminished images of the elements of the scene, and presents these to our eyes as the objects for us to look at. The separations between image planes are reduced very much more than distances in these planes, the one reduction being the square of the other. Thus the compression of distances is fully explained.

Now I suggest that this explanation will not do. The correct comparison is between the unaided eye and the eye plus the telescope. The picture seems "correct" to the eye alone. With the telescope added the magnification is greater than with

the eye only, and therefore on this theory distances in the line of sight ought to appear unduly great instead of unduly small when we look through the telescope.

We can consider the matter in another way. The pictures which show the effect are not views through telescopes, but projections on a photographic plate, that is to say on a plane. The illusion, if that is the right word to use, therefore does not depend on distances between image planes at all. In fact the whole of this traditional explanation is of the *lucus a non lucendo* order. It can be formally shown to be self-contradictory by noting that we can get indistinguishable pictures by enlarging to the same size photographs taken with lenses of different focal lengths.

Clearly we can't leave the nursery yet. Let us see what a learned Oxford don has to tell the children—a U story this time.

"So she set to work, and very soon finished off the cake.

...
 'Curioser and curioser!' cried Alice (she was so much surprised, that for the moment she quite forgot how to speak good English); 'now I'm opening out like the largest telescope that ever was! Good-bye, feet!' (for when she looked down at her feet, they seemed to be almost out of sight, they were getting so far off)."

Alice, you will observe, has made the elementary deduction that because her height is increasing her feet appear to be dwindling to nothing. We can express this rather more learnedly by saying that she realized the apparent sizes of well-known objects depend on their distances. But perhaps we are no longer young enough to extract all the wisdom from Lewis Carroll's simple words.

So we must grow up, and abandon the gentle atmosphere of Oxford and the nursery for the austerities of Cambridge.

In his *Compleat System of Opticks*, a book which this year reaches the venerable age of two hundred, Robert Smith has a great deal to say about vision. In this there is nothing surprising, for in his time optical instruments generally were intended for visual use. Forgetfulness of the importance of visual instruments—they are still both economically and socially of far greater importance than all the others—is a quite modern aberration among optical writers. Parts of Smith's text are so well expressed and so apposite for my purpose that I should like to quote him at some length. He says:

"In order to account for several appearances in vision, it is necessary to consider the manner of acquiring our ideas of things by sight. The noted question proposed by Mr Molyneux to Mr Locke, whether a person blind from his birth, being made to see, could by sight alone distinguish a globe from a cube, whose difference he knew by feeling, has been pronounced in the negative by both those philosophers: and this opinion has since been confirmed by the experience of several persons, who receiving their sight from the operation of Couching, could not know any one thing from another, however different in shape and magnitude. Mr Cheselden having given us a very curious account of some observations made by a young gentleman who was couched by him in the thirteenth year of his age, I will here insert it in his own words.

Though we say of this gentleman that he was blind, as we do of all people who

have ripe Cataracts, yet they are never so blind from that cause, but that they can discern day from night; and for the most part in a strong light, distinguish black, white, and scarlet, but they cannot perceive the shape of anything: for the light by which these perceptions are made, being let in obliquely through the aqueous humour, or the anterior surface of the crystalline (by which the rays cannot be brought into a focus upon the retina) they can discern in no other manner, than a sound eye can through a glass of broken jelly where a great variety of surfaces so differently refract the light, that the several distinct pencils of rays cannot be collected by the eye into their proper foci; wherefore the shape of an object in such a case, cannot be at all discerned, though the colour may: and thus it was with this young gentleman, who though he knew these colours asunder in a good light; yet when he saw them after he was couched, the faint ideas he had of them before, were not sufficient for him to know them by afterwards; and therefore he did not think them the same, which he had before known by those names. Now scarlet he thought the most beautiful of all colours, and of others the most gay were the most pleasing; whereas the first time he saw black, it gave him great uneasiness, yet after a little time he was reconciled to it: but some months after, seeing by accident a negro woman, he was struck with great horror at the sight.

When he first saw, he was so far from making any judgment about distances that he thought all objects whatever touched his eyes (as he expressed it) as what he felt did his skin; and thought no objects so agreeable as those which were smooth and regular, though he could form no judgment of their shape, or guess what it was in any object that was pleasing to him. He knew not the shape of anything, nor any one thing from another, however different in shape or magnitude. . . . He was very much surprised that those things which he had liked best, did not appear most agreeable to his eyes, expecting that those persons would appear most beautiful that he loved most, and such things to be most agreeable to his sight that were so to his taste. We thought he soon knew what pictures represented, which were shewed to him, but we found afterwards we were mistaken: for about two months after he was couched he discovered at once, they represented solid bodies; when to that time he considered them only as party-coloured planes, or surfaces diversified with variety of paint; but even then he was no less surprised, expecting the pictures would feel like the things they represented, and was amazed when he found those parts, which by their light and shadow appeared now round and uneven, felt only flat like the rest: and asked which was the lying sense, feeling or seeing?"

The way in which we come to interpret what we see is discussed at some length. One or two later passages will serve as a summary.

"The apparent distance of an object, perceived by sight, is an idea of a real distance usually measured by feeling, as by the motion of the body in walking, or otherwise; and is suggested to the mind by the apparent magnitude of the object in view, if seen alone, (as a bird in the air, or as an object in a telescope or microscope;) but if it be seen with other objects, as it usually happens, its distance is suggested both by its own apparent magnitude and by the apparent magnitudes of other adjoining objects. . . ." (This conclusion is borne out by the slides. It is

interesting to notice that even the shadows of objects suffice to modify our impressions.)

"From what has been said it appears to me that the ideas of distance are suggested to the mind by the ideas of magnitudes of objects. Hence it follows that an object seen by refraction or reflection, appears at the same distance from the eye, as it usually does from the naked eye, when it appears of the same magnitude as in the glasses."

Now let us apply this principle to our views of cricket. We see all the figures considerably enlarged, therefore we judge they are fairly near to us. The more distant batsman appears little smaller than the bowler, and so we infer that his distance from us is but little greater. In this way we form the impression that the length of the pitch, roughly the distance between the two men, is much less than the 22 yards required by the laws of the game. This explanation is clearly just as applicable to photographs as to views seen through a telescope. (Incidentally I might remark that Smith discusses the varying appearance of the Sun at different altitudes, a matter recently considered in the correspondence columns of *Nature*. He also deals with the apparent shape of the sky, and on this too reaches a definite conclusion.)

Accepting Smith's explanation as correct, we see that Carroll has given just the least twist to the explanation of Alice's experience. When she looked down at her feet they appeared so small that she knew they must be far away. As for the dogs in the fairy tale, we judge that the soldier would appear to them just as big as a man would appear to dogs of ordinary dimensions, that is agreeably with their previous experience of mankind.

Perhaps someone is thinking, "That sort of thing may be all very well in its place, but it's psychology, not optics. In physics we are concerned only with things we can measure, and they must be measurements on which different observers will agree. Are you going to suggest that everyone will give the same answer if they are asked to say how far away someone appears to be when he is seen through a telescope?" The question is obviously important. Let us hear what we can quote from Robert Smith in reply to this. (See diagrams reproduced in figure 1.)

"An object seen by refraction or reflection, appears at the same distance from the eye, as it usually does from the naked eye, when it appears of the same magnitude as in the glasses. To determine this distance in all cases, I conceive a ray OA to go from the eye at O , and after its last reflection or refraction to belong to the focus o , in the common axis OCQ of all the surfaces; and to meet an object PQ in P , placed perpendicular to OQ ; and that a line $P\omega$ is drawn parallel to the axis OQ till it meets the ray OA , produced, in ω . Then supposing the object PQ to be removed to the place $\omega\chi$, and there to be viewed by the naked eye; since it appears under the same angle $\omega O\chi$ or AOC as it appeared under in the glasses, when it was at PQ , it will also appear of the same magnitude and consequently at the same distance from the eye in both cases. . . ."

Smith goes on to name $O\chi$ the apparent distance of the object PQ , and $\omega\chi$ the apparent object. It should be particularly noted, since it is so opposed to ideas

prevalent to-day, that the apparent object differs both in size and position from the image presented as the immediate object to our eyes. We may at times have wondered at the ineptitude displayed by students trying to put a pin in the right place to mark the position of an image; if so it has not occurred to us that our surprise could be more appropriately attributed to errors we have cherished in our own minds.

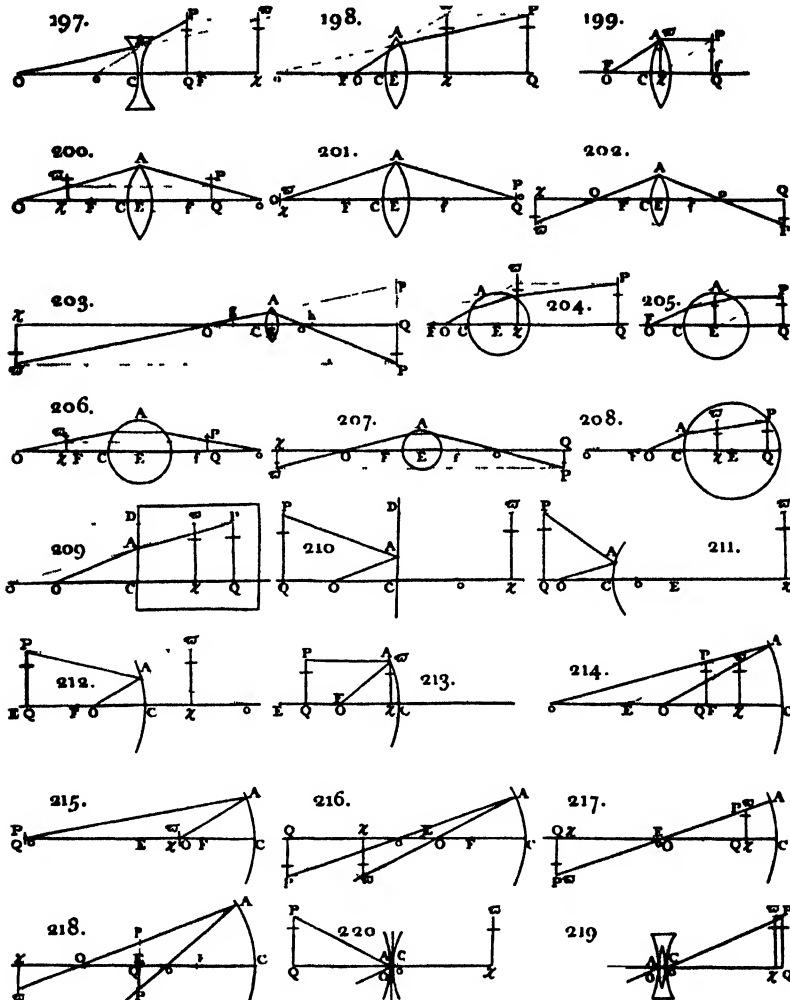


Figure 1.

Though we still retain the name geometrical optics, nowadays we prefer the algebraic to the geometrical form. Let me then recall our procedure briefly. At a refracting or reflecting surface a ray undergoes a change of direction represented by the product of the power of the element and the distance of the point of incidence from the axis. Between successive surfaces the direction remains constant but the

distance from the axis changes. On these two facts we are led, in any instrument symmetrical about an axis, to equations of the form

$$\begin{aligned} -\xi' &= ax + b\xi, & -\eta' &= ay + b\eta, \\ x' &= cx + d\xi, & y' &= cy + d\eta, \end{aligned}$$

where x, y are the displacements from the axis of the point in which the ray meets the first surface, and x', y' the corresponding co-ordinates at the last surface; ξ, η are the increments in the x and y co-ordinates as we proceed through unit distance along the incident ray away from the system, and ξ', η' are similarly defined for the emergent ray. The quantities a, b, c, d are definite functions of the powers of the individual surfaces and of their optical separations. The four are not independent, but satisfy the relation $bc - ad = 1$. It follows that the equations can be solved in the form

$$\begin{aligned} -\xi &= ax' + c\xi', & -\eta &= ay' + c\eta', \\ x &= bx' + d\xi', & y &= by' + d\eta'. \end{aligned}$$

Now suppose that the incident ray passes through a point (X, Y) distant u from the first surface, and the emergent ray through (X', Y') at a distance v from the last surface. Then

$$-\xi' = AX + B\xi, \quad -\eta' = AY + B\eta \quad \text{.....(i),}$$

$$X' = CX + D\xi, \quad Y' = CY + D\eta \quad \text{.....(ii),}$$

and

$$-\xi = AX' + C\xi', \quad -\eta = AY' + C\eta' \quad \text{.....(iii),}$$

$$X = BX' + D\xi', \quad Y = BY' + D\eta' \quad \text{.....(iv),}$$

where

$$A = a \quad \text{.....(v),}$$

$$B = b - au \quad \text{.....(vi),}$$

$$C = c - av \quad \text{.....(vii),}$$

$$D = d - cu - bv + auv \quad \text{.....(viii).}$$

From (v) A is a constant of the system. It will be recognized as the power: for instance if $A = 0$, equations (i) show that corresponding to parallel incident rays we have parallel emergent rays; that is to say the system is telescopic. B is clearly the angular magnification. From equations (ii) $D = 0$ is the condition that u, v determine a pair of conjugate points, and C is the linear magnification of the image at v . Now if we place our eye at the point $X' = Y' = 0$ and look at an object extending from (X, Y) to the axis, Smith's definition says the apparent distance is δ where $X = -\delta\xi'$, $Y = -\delta\eta'$. It follows from (iv) that $\delta = -D$. The negative sign arises because our standard direction for measuring distances is away from the lens, whereas Smith takes his positive direction as that in which he is looking, that is towards the instrument. With our conventions the apparent distance of the object is D .

At this stage we may note that our Physical and Mathematical statements of the problem have met. Instead of $\frac{1}{u} + \frac{1}{v} - a$, (viii) shows that the form which always has a real meaning is $u + v - auv$, and this meaning, as we have seen, is particularly important in the theory of visual instruments.

In most instruments, when three of the quantities A, B, C, D or a, b, c, d are known, the fourth can be found from the relation $BC - AD = 1$ or $bc - ad = 1$: this is the only procedure left to us if we follow many of our present-day text books, but this method fails to give D when A is zero, that is to say when the instrument is a telescope. The omission to consider this quantity when dealing with telescopes is clearly a serious fault. It is analogous to a disregard of the power or focal length in instruments of other kinds. The only telescope users who are not concerned with D are the astronomers; for the objects they deal with are so remote that to talk of their apparent distance is meaningless.

In a telescope magnifying m times, equation (viii) gives

$$D = d - \frac{u}{m} - vm.$$

As the observer's eye is placed close to the instrument, the only variable quantity is u , and the equation indicates that the essential property of a telescope is to make objects appear nearer. (The name suggests this. Just as a microscope is an instrument for looking at objects so that they no longer appear inconveniently small, so a telescope is for looking at objects so that they no longer seem inconveniently far away.) The conversion of real into apparent distances involves a uniform compression inversely proportional to the angular magnification; this ratio is quite different from that which holds for the separation of images.

There is one more result—one that still seems rather surprising though it has been known for more than two hundred years—that I must not fail to mention. It is due to Cotes. I suppose most of us have sometimes looked through a telescope the wrong way round. Everything then appears diminished or more distant, instead of nearer and so larger. If two men were looking at one another at the same time through the same instrument we should accordingly expect them to appear of very different sizes. Comparison of equations (ii) and (iv), or the symmetry of equation (viii), shows that this expectation is wrong. The first man appears just as far from the second as the second does from the first, and therefore the magnification is the same for both. The key to the paradox lies in the fact that the experiments we usually carry out do not correspond to the conditions assumed in the theory: we do not simply interchange the positions of the observer and the person observed.

Now perhaps someone may feel inclined to ask, why, if an instrument such as a telescope gives the same magnification both ways round, we don't use it in both ways. The answer is in two parts. Firstly utilitarian considerations lead us to prefer one alternative to the other. Let us imagine at a theatre an audience of undergraduates who only know of the other way of using opera glasses. Each of them would be brandishing his glasses at the end of a pole or other contrivance to bring them close to the particular feature of the actress of which he was enamoured, or at least desired to get a much better view; let us, following authority, say her eyebrow. The competition for attaining the desired position of the glasses will mean that most of the audience become disgruntled, and even the actress may not get all the

pleasure from it that she should. Hence sensible people take the other alternative, which ensures the greatest happiness for the greatest number.

The second part of the answer is that we do turn the telescope round in this way, but we then give it a different name: we call it a microscope. It was to be expected that the microscope and the telescope should be practically simultaneous inventions. As this use of a reversed telescope is not familiar I have included among the exhibits a telescope used as a microscope.

So far I have confined myself to the particularly simple side of geometrical optics which is regarded as suitable for presentation to the average boy or girl in our schools. My purpose has been to show that if we fail to take into account the idea of apparent distance we are omitting something of real educational value; in fact we are failing to make use of the child's ordinary experience of his surroundings and of what he is most likely to have observed for himself in his private and possibly surreptitious optical experiments; and the theory we present to him is incomplete, unsymmetrical and distorted. I can imagine many teachers loath to abandon

$$\frac{1}{u} + \frac{1}{v} = \frac{1}{f}$$

as the standard form of equation. I think they assume it is more quickly solved than the corresponding form $D=0$. This may be the case if students are supplied with a good table of reciprocals to save arithmetical labour, but I expect this would, to say the least, be abnormal. Failing these tables the alternative form of equation seems to have a slight advantage.

I wish now to discuss briefly the extension of the elementary theory to systems not having symmetry about an axis. Lenses of this class are used very widely in spectacles, so the theory should be regarded as of general interest. I very much doubt though whether many of our opticians or oculists understand much about these systems. As a rule they refrain from thinking of two cylinders unless their axes are in the same plane, and they probably proceed chiefly by rule of thumb, applying the theory of symmetrical instruments in the two principal planes.

Now in fact the theory of unsymmetrical instruments is not particularly difficult—far less difficult than is usually supposed. There is no reason why anyone of ordinary ability should not be able to deal with systems incorporating cylinders with their axes arranged in arbitrary positions. The theory can, in fact, be presented in a form differing remarkably little from that for symmetrical systems. The difference appears in the calculation of the four magnitudes a , b , c , d . Instead of being numbers of the familiar type—quantities of the kind the mathematician calls scalars—each is a combination of two vectors. We can deal with any problem we are likely to meet when once we have realized the nature of these vectors and the way they are added and multiplied.*

Before I state what these laws of combination are, it may not be out of place to compare the symmetrical class with the unsymmetrical. I think the former might be described as staid and respectable—almost uninteresting. This cannot be said

* For the theory see Appendix I.

of the other class. If you have been interested in the Hall of Mirrors at Madame Tussaud's—perhaps one of the best equipped laboratories for teaching the elements of optics in existence—you may agree with me that unsymmetrical instruments are entertaining but neither respectful nor respectable. Some excuse can be offered for them. When they present a man with a view of himself suggestive of a complacent but not contemplative Buddha, with, in place of legs, a rounded base as though he were an outsize in paper weights, they are only doing the kind of thing that was done earlier at Oxford. And we can apply what we have learnt about *D*, for instance the reciprocity law, even to these grotesque pictures.

For instance if a man, entertaining his small son with the distorting mirrors, stands, with the boy before him, in front of a mirror of the character I have just described, we may expect that while the father surveys approvingly the modification of his nether regions, the son, unseen, is agitated by the unexpected disappearance of his father's head.

If we will listen, our Oxford philosopher tells us all this plainly enough, and even goes farther: "How are you getting on?" said the Cat, as soon as there was mouth enough for it to speak with.

Alice waited till the eyes appeared, and then nodded. "It's no use speaking to it", she thought, "till its ears have come, or at least one of them."

Misfortunes such as these arise from one part of the body appearing at a very different distance from another part. It is not the kind of thing for the oculist to imitate. We can lay it down that his mission is to enable us to see the different parts of any sufficiently small object at the same apparent distance; and this distance should be the same for all rays entering the eye. We cannot discuss this until we know how to find *a*, *b*, *c*, *d* when the system is not symmetrical. The process involves both the addition and the multiplication of cylindrical powers. When we investigate these processes it immediately appears that the analysis into spherical and cylindrical components is wrong—that is to say it is not the resolution which leads, so far as the optical effects are concerned, to simple intelligible computation or interpretation. It may be the right form of instruction to give to the workman who is to make up the spectacles, but it is certainly not the best form for prescribing them. The relation between the mechanical and scientific systems, as I will call them, is shown in the following table, where the variables *S* and *C* signify the quantities regarded as the essential components at the present time.

Table 1. Specifications of spectacle lenses in the mechanical and the scientific systems

Mechanical system			Scientific system		
D.Sph.	D.Cyl.	Axis	D.Sph.	D.Ast.	Axis
+S	+C	n°	$+S + \frac{1}{2}C$	$\frac{1}{2}C$	n°
+S	-C	n°	$+S - \frac{1}{2}C$	$\frac{1}{2}C$	$(90 + n)^\circ$
-S	+C	n°	$-S + \frac{1}{2}C$	$\frac{1}{2}C$	n°
-S	-C	n°	$-S - \frac{1}{2}C$	$\frac{1}{2}C$	$(90 + n)^\circ$

The correct division is into a spherical component of power equal to the mean of the principal powers, and therefore also to the mean of the powers of any two perpendicular sections, and an astigmatic component. The latter will perhaps be most readily understood if I describe it as a combination of two equal cylinders, of opposite signs, with their axes at right angles. The power of the astigmatic lens is numerically equal to that of either cylinder. If its axis is taken to be that of the positive component its sign will always be positive.

It should be observed that with this system every specification is unique. There is only one way of writing it. Consequently the subject of the transposition of prescriptions disappears. In what follows I shall use the scientific system, denoting the magnitude of the spherical component by S and that of the astigmatic component by X .

That this is the correct method of analysis of a mixed lens seemed so obvious that I had a shock when a passage in a book by one of my optical friends implied, as I thought, that Stokes held a different opinion. But reference to Stokes' paper showed that my fear had been needless; the term astigmatic lens, which I have used to designate the non-spherical component, is the expression employed by Stokes, and was presumably coined by him.

The vector construction for the addition of astigmatic lenses which is given in ophthalmic text books, is originally due to Stokes, though sometimes attributed to others. The essential feature is that the angle of the optical vector is double the angle of the lens axis. (See Appendix I.) Exactly the same law holds for the spherical components also.

If the last statement seems surprising it is only because the vector nature of spherical power has not been realized. An alteration in its angle implies a rotation of the image field relatively to the object field. Rotation of this kind is easily taken into account when we build up our theory on the changes suffered by a typical ray; but less easily and naturally, I should expect, on the curvature system. It should be interesting to know how those who use this system exclusively would discuss this property with their pupils.

How a spherical power comes to have an angle associated with it appears from the law for the multiplication of powers, which may be stated as follows:

To ascertain the nature of any product only the astigmatic factors are considered. The product of an even number of astigmatic factors is of spherical type, that of an odd number is astigmatic. The angle associated with any product is a function of the angles of the elementary astigmatic components. It is equal to the angle of the last component minus the angle of the preceding combination. Thus if ϕ_r is the angle of the astigmatic power X_r , the angle θ of a spherical contribution containing astigmatic factors $X_1, X_2, X_3 \dots X_{2n}$ is given by

$$\theta = -\phi_1 + \phi_2 - \phi_3 + \dots + \phi_{2n},$$

and the angle ϕ of an astigmatic contribution containing the factors $X_1, X_2, X_3 \dots X_{2n+1}$ by

$$\phi = \phi_1 - \phi_2 + \phi_3 - \dots + \phi_{2n+1}.$$

Let us apply the angle law in some simple cases. If we look through an instrument at a line (which counts as an astigmatic element) inclined at an angle α with the axis, the inclination β of its image will be determined by prefixing the angle α to θ or ϕ as the case may be. Thus in an instrument of spherical type

$$\beta = \alpha + \theta,$$

and in one of astigmatic type

$$\beta = \phi - \alpha.$$

Now suppose the instrument is kept stationary and the object rotated—say α is continuously increased; the object and image will revolve in the same sense if the instrument is of the spherical type, and in opposite senses if it is of the astigmatic kind, corresponding to increasing and decreasing values of β respectively.

In instruments having components of both kinds, superposition of these opposing effects tends to cause a confused image; unless the rays are selected in some way, as for instance by a small stop, only lines running in two fixed directions at right angles to one another are sharply defined.

Again if the object is fixed and the instrument is rotated, the angle ϕ of each astigmatic lens is increased by twice the angle of rotation, say χ . In θ the number of ϕ 's is even, and half occur with positive and half with negative signs. It follows that θ is unaltered by rotation of the entire instrument, and hence β is also unchanged. In ϕ on the other hand the positive terms number one more than the negative terms, and ϕ therefore increases by 2χ . Since β increases by the same amount as ϕ , the image in the astigmatic case revolves twice as rapidly as the instrument and in the same sense.

As a rule in instruments containing astigmatic lenses both effects are present simultaneously, and what we see depends on the relative magnitude of the two. When an optician examines a lens he finds whether a cylindrical correction has been incorporated by looking through the lens at perpendicular cross lines while he rotates it about its axis. The apparent position of the object of course depends on the function D .* If the apparent direction of the cross lines does not change the lens surfaces are spherical; if a cylindrical component is present he expects to find what he calls the scissors movement—the lines have a to and fro angular motion like the blades of a pair of scissors in use. But this is only part of the story. By making a suitable choice of object and lens distances we can alter the relative magnitude of the spherical and astigmatic components of D almost as we like, and instead of the scissors movement we can cause the lines as seen through the lens to perform complete revolutions. We can obtain both effects simultaneously by using two different distances, e.g. cross lines near to the lens and any remote object. The cross lines will then show the scissors effect while the trees and buildings in the distance turn somersaults. Figure 2 shows the changes of apparent direction of perpendicular cross lines with a simple cylindrical lens. The change from oscillation to continuous rotation is particularly interesting.

* In the general case apparent position seems more appropriate than apparent distance, since apparent rotation of the object is included in D .

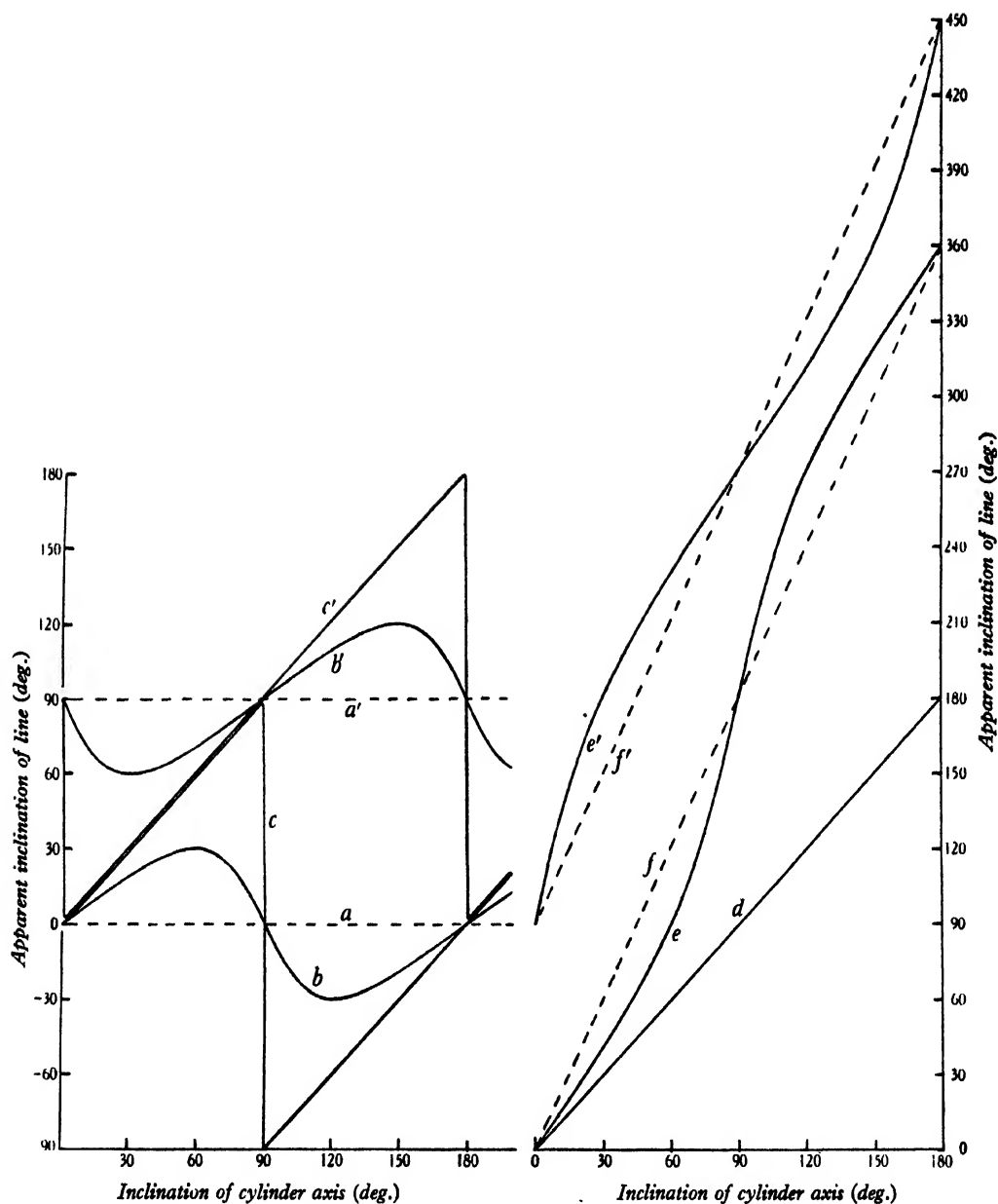


Figure 2. *The scissors effect and its variations.* The lens is a cylinder of power 2, i.e. $S=1$, $X=1$. The distance of the observer's eye from the lens is $\frac{2}{3}$. a, a' , cross lines in contact with lens: spherical effect. b, b' , cross lines distant $\frac{2}{3}$ from lens: scissors effect. c, c' , cross lines just less than 2 from lens: limiting form of scissors effect: both lines parallel to lens axis. d , cross lines just more than 2 from lens: both lines parallel to lens axis: continuous rotation begins. e, e' , cross lines at infinity: oscillation superposed on continuous rotation. f, f' , the pure astigmatic effect: cross lines appear to rotate twice as fast as the lens: only attained with a virtual object under the conditions assumed here.

As far as I know the first instrument made to exhibit the rotational property was constructed by Burch of Reading University College. It consisted of two (equal) cylindrical lenses with their axes parallel, separated by a distance equal to the sum of their focal lengths. I have an illustrative model. It does not produce sharp images because Burch failed to take apparent distance into account. Consequently there is a large amount of astigmatism: the images of lines in the two principal planes of the telescope are twice the length of the instrument apart. The same defect appears in other instruments described in the same paper. Burch must have possessed remarkable powers of accommodation, not to mention tolerance of astigmatism, to be able to use these instruments in some of the ways he describes.

A true astigmatic instrument—we might perhaps say a panastigmatic instrument—must have all the four quantities A, B, C, D of the pure astigmatic type. This involves at least three lenses, each as a rule with both spherical and astigmatic components. A simple unit power telescope of this kind can be made with three similar lenses with their axes parallel, and each separation equal to the focal length of the astigmatic component and to twice that of the spherical component. Real images can be obtained. For instance the object and image planes can each be one quarter the length of the whole instrument from the extreme lenses. As all the axes lie in one plane it is easy to verify that this construction gives the properties mentioned.

Another interesting system is of the spherical type, but the images are neither inverted nor erect. This effect can only be obtained by adjusting the axes of the astigmatic components to lie in different planes. At least four component lenses are necessary. A unit telescope can be made from four similar lenses spaced at equal intervals. To secure an image rotated through an angle ϵ relative to the object the axis of each lens should make an angle $\frac{1}{4}(\pi - \epsilon)$ with that of the preceding lens. Taking the separation between the lenses as the unit of length, the power of the spherical component should be 2 and that of the astigmatic component $(2 \sin \frac{1}{2}\epsilon)^{\frac{1}{2}}$. The range of possible constructions is shown in figure 3. For instance to turn the image through a right angle the axes of successive lenses make angles of $22\frac{1}{2}^\circ$, and the powers are 2 spherical and $2^{\frac{1}{2}}$ astigmatic. In the notation of the optician the specification would be $2 - 2^{\frac{1}{2}}$ spherical, $2 \times 2^{\frac{1}{2}}$ cylindrical, a ratio of about 15 : 44 or approximately 1 : 3. If we put two telescopes of this kind in series we rotate the image through two right angles, that is to say we apply the factor -1 . The single telescope therefore is a representation of $\sqrt{-1}$. I should get into trouble with my mathematical friends if I called it i , so I will go as far as I dare and suggest the name j .

Though it would be a mistake to assume that systems of the kind just considered would serve no useful purpose, we have to realize that the study of astigmatism is chiefly pursued with the intention of eliminating it, or at least of compensating for its presence. In the most important case which calls for consideration there are only two astigmatic components. From what has been said already it is obvious that the axes of these components will be either parallel or perpendicular.

Suppose the two components, say X and X' , are separated by a symmetrical

system represented by the functions a, b, c, d . When the astigmatic components are included these are replaced by a^*, b^*, c^*, d^* , where

$$a^* = a + Xb + cX' + XdX',$$

$$b^* = b + dX',$$

$$c^* = c + Xd,$$

$$d^* = d.$$

From these equations it is obvious that the astigmatic lenses can only neutralize one another if $d=0$, that is to say if the one lens is situated at a real image of the other. This result is important.

2.0 \overline{S}

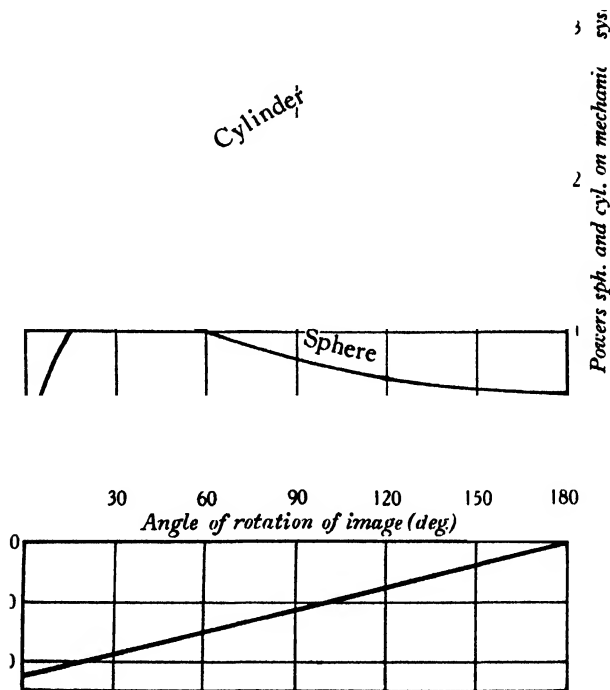


Figure 3.

Let us first consider it from the point of view of the instrument maker. We learn from it that, as a rule, a fault which is remediable by figuring a surface can only be perfectly corrected by working one particular surface, which is the one where the error arises. It has to be remembered that the formation within an instrument of real images of its components is exceptional. It is true that correction can be secured by working several surfaces no one of which is imaged on another,

but as the method of doing this involves preliminary theoretical investigation it can hardly be regarded as a suitable alternative for the workshop.

In addition to the vanishing of d the relation $Xb + cX' = 0$ must be satisfied. Since in this case we have $bc = 1$ the correcting power X' is given by $X' = -Xb^2$. The negative sign indicates that the axes of the two astigmatic lenses must be perpendicular to one another. It will be recalled that b represents the angular magnification. This astigmatic theory is of course relevant to the design of such instruments as photographic lenses, where astigmatic differences of power arise owing to the obliquity of the incidence of light on the surfaces. One of the exhibits shows the astigmatic effect of a tilted spherical lens. The object as seen by light passing outside this lens remains stationary as the instrument is rotated; but as seen through the lens it exhibits the rotation characteristic of an astigmatic lens.

From the point of view of the oculist the condition $d = 0$ implies that astigmatism due to want of sphericity in the cornea can only be fully corrected by means of contact glasses or alternatively by appliances far more clumsy than spectacles. The oculist has also to remember that the eye rotates to some extent in its socket in the course of its normal movements. When investigating what form of spectacle lens will give the most satisfactory vision, the inclination of the axes of the astigmatic components of the lens and of the eye on its extreme excursions should be taken into account. The general theory of astigmatic systems is therefore required for a full understanding of common spectacle problems. It is also necessary for others with which I have not attempted to deal—for instance the way in which judgment of distances on the principle considered here is modified for near objects by binocular vision, and the effect of glasses for players in games such as cricket and lawn tennis, where the path of a ball in rapid motion has to be recognized. These fall outside the limits of the elementary theory to which I am restricting myself to-night.

I can however give some examples of the application of the theory to simple instruments. I take reflecting telescopes of unit power as illustrations. Spherical mirrors can be employed, since astigmatic powers are introduced by letting the light fall obliquely on the surfaces. I select three types, which may be named the *chimney*, the *cube*, and the *steps* respectively. As with all other telescopes it is insufficient for clear vision through them to ensure that parallel incident rays emerge in parallel directions and that the magnification shall not vary for rays in different planes. In addition to these conditions it is essential to control the apparent position. In all three examples this has been done by making the apparent distance D zero for an object distant t in front of the first mirror and a real image distant t from the last mirror. Perhaps I might remark here that it is often not realized that a telescope can form real images of objects within a limited distance of the instrument. For example it is possible to use a telescope to project pictures on a screen.

The *chimney* telescope may be represented symbolically by the expression

$$\left[t \begin{pmatrix} P \\ S \end{pmatrix} t \right]^n,$$

which implies a succession of n systems, each of the type indicated by the letters

within the square brackets. The t denotes a distance measured along a principal ray, so that $2t$ is the distance between the vertices of successive mirrors. The p and s denote the primary and secondary planes of reflection; the events which occur to rays in one plane are shown in the upper position, and those experienced by rays in a perpendicular plane in the lower position. In this expression all the p 's occur at one level, and all the s 's at another level. This implies that all the mirror vertices and centres of curvature lie in a single plane. The regular formations have the vertices either on two parallel straight lines or at the corners of a regular polygon. The chimney describes the former. The path of the ray reflected at the vertices of the mirrors is shown in figure 4.

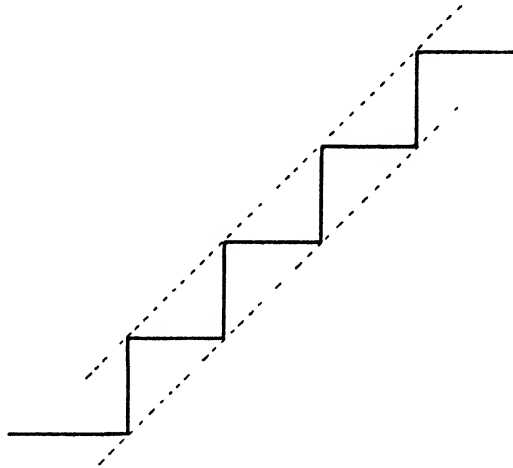


Figure 4. Path of central ray in chimney reflecting telescope.

The system is severely limited in its degrees of freedom. If r is the radius of each mirror and $\pi - 2\delta$ the deviation suffered by the central ray at each reflection, we must have

$$\cos \delta = \frac{\sin \frac{h\pi}{2n}}{\sin \frac{k\pi}{2n}},$$

$$\frac{t}{r} = \sin \frac{h\pi}{2n} \sin \frac{k\pi}{2n},$$

where h and k are integers. If h and k are both even, the telescope is erecting; if both odd, inverting; and if one is odd and one even it is panastigmatic.

The next construction is represented by

$$\left[t \begin{pmatrix} p \\ s \end{pmatrix} 2t \begin{pmatrix} s \\ p \end{pmatrix} t \right]^n.$$

Rays in the primary plane for one reflection lie in the secondary plane at the next. Consequently we cannot have more than three consecutive mirror vertices in the

same plane, and the plane containing those of mirrors 2, 3, 4 is perpendicular to the plane in which those of mirrors 1, 2, 3 lie. If the deviation is a right angle one regular arrangement leads to the central ray tracing out a number of the edges of a cube, as shown in figure 5. The conditions for clear vision are less restricted than in the previous telescope. They only amount to the one relation

$$\frac{4t}{r} = \cos \delta + \sec \delta \pm \left\{ \cos^2 \delta + \sec^2 \delta + 2 \cos \frac{h\pi}{n} \right\}^{\frac{1}{2}},$$

where h is not zero or a multiple of n . The telescope is inverting or erecting according as h is odd or even. The astigmatic variety is ruled out.

The third type is represented by

$$\left[t \begin{pmatrix} p \\ s \end{pmatrix} 2t' \begin{pmatrix} s \\ p \end{pmatrix} 2t \begin{pmatrix} s \\ p \end{pmatrix} 2t' \begin{pmatrix} p \\ s \end{pmatrix} t \right]^n,$$

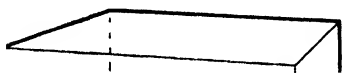


Figure 5. Path of central ray in cube reflecting telescope.



Figure 6. Path of central ray in steps reflecting telescope.

and it is easy to verify that if we divide the system after any even number of reflections the next four mirrors will have their vertices in a single plane, and that at the next division the new plane will be perpendicular to its predecessor. One arrangement of the path resembles a short flight of stairs in outline, hence the name proposed. In addition to other solutions we get an erecting telescope for all values of n if we make

$$r (\cos \delta + \sec \delta) = 2t (\cos^2 \delta + \sec^2 \delta) = 4t'.$$

Although all these telescopes satisfy the conditions for clear vision by rays near the central ray, they will be found to behave very differently with large fields of view. The chief factor which makes for good vision over a large field is symmetry. It is not an unprofitable study to consider how one system differs from another in this respect. Among the systems I have described the best definition has been obtained with the steps; it may be arranged (see figure 6) as steps up one side of a

wall and down the other, a mirror on one side being exactly opposite a mirror on the other side. The worst results have been found with the chimney arrangement.

If some of the systems I have described appear to you to be rather fantastic creations, I would say that situations have arisen where they can be usefully applied, and I have no doubt that other uses for such instruments will be found.

In conclusion I must express my thanks for the assistance I have received from many helpers. To Mr Philpot, director of the British Scientific Instrument Research Association, I am deeply indebted for the aluminizing of the mirrors used in the reflecting telescopes. Colleagues at the National Physical Laboratory have helped in numerous ways: it is only fitting that I should mention in particular Dr Anderson, Mr Buxton, Mr Pinfold and Mr Turl, without whose assistance I should not have been able to bring these model systems for you to see. For several of the pictures I have shown on the screen I am indebted to the two youngest members of my family.

APPENDIX I

If in the second order surface equation

$$2z = ax^2 + 2bxy + cy^2,$$

we write $x = r \cos \psi$, $y = r \sin \psi$, we obtain an equation of the form

$$\frac{2z}{r^2} = \frac{a+c}{2} + d \cos 2(\psi - \chi),$$

where χ is the angle of a principal section. Since power depends on the rate at which the path length varies with r^2 , it follows that the power of a single surface is of the form $S + X \cos 2(\psi - \chi)$. The optical angle is thus twice the mechanical angle.

If two surfaces of this type occur in contact, the optical path at (r, ψ) is the sum of those of the elements. It at once follows that the laws for the addition of powers are

$$S = S_1 + S_2,$$

$$X\{\phi\} = X_1\{\phi_1\} + X_2\{\phi_2\}, \quad \phi = 2\chi,$$

where the second equation implies that the addition is vectorial. This construction, first given by Stokes, is illustrated in figure 7.

Since the normal at (x, y) has direction cosines in the ratios $ax + by$, $bx + cy$, -1 , the directions of a ray refracted at this point satisfy

$$\frac{\xi' + \xi}{ax + by} = \frac{\eta' + \eta}{bx + cy} = -(\zeta' + \zeta) \simeq \mu - \mu';$$

these equations are a simplification of the more general type

$$\begin{aligned} -\xi' &= \xi (b \cos \beta + b' \cos \beta') + \eta (-b \sin \beta + b' \sin \beta') \\ &\quad + x (a \cos \alpha + a' \cos \alpha') + y (-a \sin \alpha + a' \sin \alpha'), \\ -\eta' &= \xi (b \sin \beta + b' \sin \beta') + \eta (b \cos \beta - b' \cos \beta') \\ &\quad + x (a \sin \alpha + a' \sin \alpha') + y (a \cos \alpha - a' \cos \alpha'). \end{aligned}$$

Assume that this form holds for each of two parts of a complete system. The equations connecting the variables in the two parts are

$$\xi_1' + \xi_2 = \eta_1' + \eta_2 = 0, \quad \frac{x_2 - x_1}{\xi_1'} = \frac{y_2 - y_1}{\eta_1'} = \frac{t}{\mu},$$

where t is the length of the path between the components in the intervening medium of index μ .

In the expression for ξ_2' , η_2' in terms of ξ_1 , η_1 , x_1 , y_1 , derived by eliminating the remaining variables, the coefficients of x_1 and y_1 clearly contain terms having $\frac{t}{\mu}$ and an a from each component as factors. Considering these terms alone it is easy

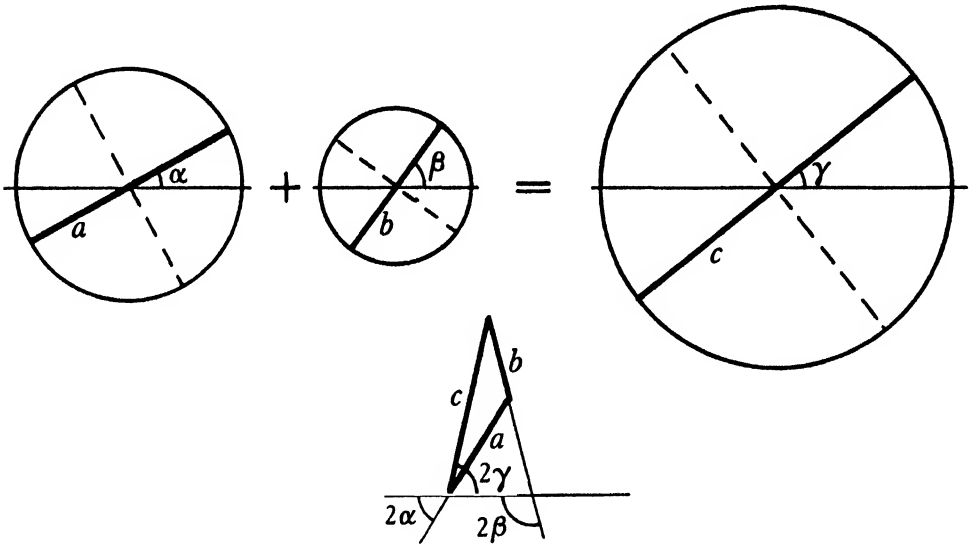


Figure 7. Stokes' construction for the addition of astigmatic powers.

to verify that they make contributions to ξ_2' and η_2' of the same type as has been assumed for each part. If we denote these types by the notations $a(\alpha)$ and $a'\{\alpha'\}$ respectively, the terms we are considering are $\frac{t}{\mu}$ times

$$a_1 a_2 (\alpha_2 + \alpha_1) + a_1' a_2 \{\alpha_2 + \alpha_1'\} + a_1 a_2' \{\alpha_2' - \alpha_1\} + a_1' a_2' (\alpha_2' - \alpha_1').$$

This shows that the products $a_1 a_2$ and $a_1' a_2'$ are of the kind characteristic of the spherical group, and $a_1' a_2$ and $a_1 a_2'$ of the other, the astigmatic group.

When we are dealing with individual surfaces, the angle for each spherical component is zero. It readily follows from the equations we have found for combining angles that in all groups the resultant angle is obtained by summing the angles of the astigmatic factors with their signs alternately positive and negative when arranged in their proper order, the sign of the final term being always positive.

APPENDIX II

As the representation of the properties of optical systems of the most general kind by vectors of two distinct groups enables graphical methods to be employed, and as the procedure is new, it may be helpful to portray the stages by which the properties of the telescope mentioned on p. 879 are reached. This has been done in

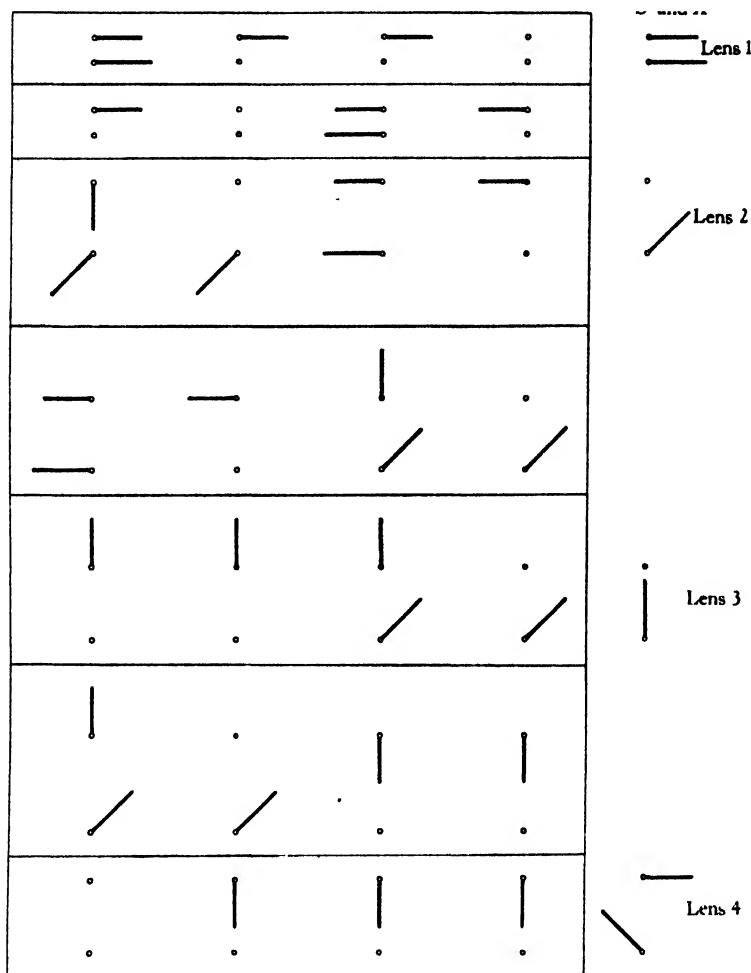


Figure 8. Graphical representation of the action of telescope 'j'.

figure 8, each stage being represented by a separate scene. Instead however of taking the displacement from one lens to the next as an elementary event, it has been replaced by the joint effect of

- (i) half the spherical power at the beginning of the interval;
- (ii) the displacement;
- (iii) half the spherical power at the end of the interval.

The joint effect of the three is to replace A, B, C, D by $C, D, -A, -B$ respectively. All that is left is to combine the effects of the remaining half of the spherical powers of the external lenses, and the astigmatic effects of all. The insertion of these powers does not alter C and D , but the products of the power to be included and C and D respectively are to be added to A and B . The directions ascribed to the vector products are to be determined by the rules stated on p. 876.

In figure 8 the spherical components of each of the four quantities A, B, C, D are given immediately above the astigmatic components. To begin with we have the representation of free space—unit vectors for B and C in the upper line and all else zero. The powers to be incorporated are represented on the extreme right. Multiplying C and D by these has the effect, shown in the first scene, of adding these powers to A . This gives the initial A and B . In accordance with the explanation just given, the four actors first posing as A and B , having made their bow, subsequently stand on their heads and in this posture walk through the next three scenes, making a half-right turn on going from one scene to the next. Before they finally disappear they help to determine the character of their successors.

For instance a particular A and B make their last appearance in scene two. Their successors in scene three differ from them by the product of the astigmatic power shown on the right and C and D . The non-zero elements of C and D have the angle π , and that of the power to be introduced is $\frac{1}{4}\pi$. The vector additions to scene two therefore lie in the direction $\frac{1}{4}\pi - \pi$, or $\frac{3}{4}\pi$. In magnitude the spherical components of C and D are equal to unity, and the astigmatic components of the new A and B are therefore $2\frac{1}{2}\{\frac{3}{4}\pi\}$, since the old values are zero. The astigmatic components of C and D are of magnitude $2\frac{1}{2}$ and 0 respectively. After multiplication by the new power the contributions to A and B are respectively $2\frac{1}{2}\{\frac{3}{4}\pi\}$ and 0. Adding these to the previous values 1 (0) and 0 we get the components 1 ($\frac{3}{4}\pi$) and 0 shown in the diagram. The other stages should be followed readily enough by similar treatment.

It will be realized that in practice the work would be abbreviated by cutting out the repetitions which occur. The figure contains almost four times as many representations as are necessary.

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THE FOCUSING PROPERTIES OF THE ELECTRO-STATIC FIELD BETWEEN TWO CYLINDERS

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ABSTRACT. A general survey of the focusing properties of an electron mirror formed by two cylinders has been made. Photographs of the images formed are shown, and the relation between object and image distances for different voltage ratios on the cylinders are obtained. A special case of multiple reflections is described. Some qualitative results relating to the behaviour of the two-cylinder lens at very high voltage ratios are given, and the formation of intermediate images in both lenses and mirrors is discussed. Finally, a qualitative description of the focusing properties of two cylinders for voltage ratios from $-\infty$ to $+\infty$ is given.

§1. INTRODUCTION

SEVERAL papers^(1,2,3,4,5,6) dealing with the electron mirror have already appeared. These have in general, however, been concerned with the Einzel lens and its corresponding mirror. A more recent paper⁽⁷⁾, which was published during the preparation of the present one, has, however, included the case of a cylinder and a plane or curved electrode. The Einzel lens is one of the most complicated types, since under certain conditions the field near the axis behaves as a lens, while the field near the electrodes behaves as a mirror. Moreover, when the system finally becomes entirely a mirror the range of focal lengths is still rather limited. In the following work a very simple case, the mirror formed between two cylinders, has been chosen for investigation. This arrangement lends itself readily to experiment, and the results, together with some recent results relating to the lens formed between two cylinders, fill in the gaps in our knowledge of the focusing properties of two cylinders maintained at different potentials. The focusing properties of the lens formed between two cylinders have been studied over a limited range by Epstein⁽⁸⁾, and a later paper by Klemperer and Wright⁽⁹⁾ includes the case of decelerating lenses. No measurements have yet been published for the case in which the final cylinder is maintained at a negative potential with respect to the cathode, or for that of very high potential ratios on the two cylinders. The first of these constitutes the electron mirror and the second is concerned with the formation of intermediate images in lenses. The electron mirror will be dealt with first.

§2. THE TWO-CYLINDER ELECTRON MIRROR

Consider two cylinders, figure 1 A, with an electron beam entering from the left. The cylinder on the right is maintained very much negative to the cathode, while the one on the left is maintained positive. Under these conditions a zero

equipotential surface is formed in the region within the two cylinders, and its exact location can be determined by means of a field plot in an electrolytic trough. The beam of electrons travelling to the right in this system is first decelerated and then returned towards the cathode, the direction of each ray being determined by the angle of incidence and the shape of the equipotential surfaces. This return is brought

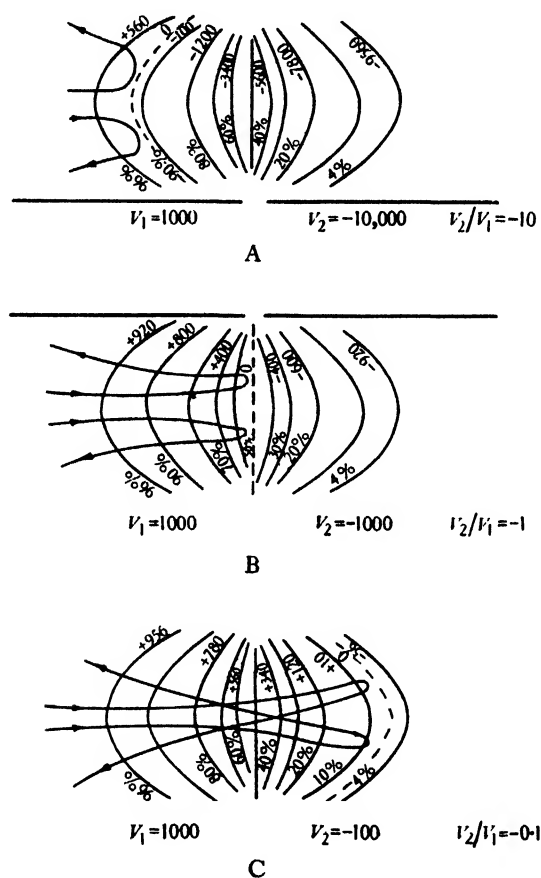


Figure 1.

about by total reflection of the electrons in the neighbourhood of the zero equipotential surface and the axially symmetric field focuses the electrons in the same manner as the field of an electron lens. The position of the zero equipotential surface can best be described as follows. It is conventional in field plots of two-electrode systems to consider one electrode at zero and to label the equipotential surfaces in terms of percentage of the total potential-difference. We can therefore in the case of the electron mirror refer the results for the two cylinders at potentials V_1 and V_2 to the case where one is at potential $(V_1 - V_2)$ and the other is at zero. The field between two equal cylinders is well known, and if we describe the zero equipotential surface in terms of it we immediately know the shape and position of

the surface. It is thus clear that when the cylinders are at potentials V_1 (positive to the cathode) and $-V_2$ (negative to the cathode) then the total potential-difference is $(V_1 - V_2)$ and any equipotential surface V_x relative to the cathode will be $(V_x - V_2)$ relative to the second electrode and hence the equipotential surface is equivalent to the 100 $[(V_x - V_2)/(V_1 - V_2)]$ per cent equipotential surface of the conventional field plot. Thus, for example, in figure 1 A where $V_1 = 1000$ and $V_2 = -10,000$ the equipotential surface $+560$ is the same as the $(560 + 10,000) \div 11,000 \times 100$, or 96 per cent equipotential surface of the conventional field plot, and the zero equipotential surface will be $(10,000 \div 11,000) \times 100$ or 90.8 per cent in the conventional field plot. The behaviour of the electron beam can in general be judged by the shape and position of the equipotential surfaces. Figure 1 A shows the approximate electron path when V_2 is strongly negative, giving a diverging field in the region through which the electron beam passes. Figure 1 B shows the path for $V_2/V_1 = -1$, in which the zero equipotential surface is midway between the cylinders, and figure 1 C shows the path of the electrons when V_2/V_1 equals $-1/10$

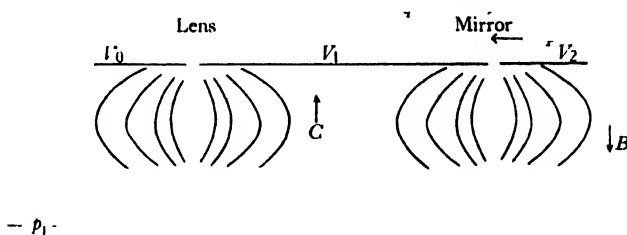


Figure 2.

and the zero equipotential surface is well within the negative cylinder. In this latter case the beam is seen to cross over once inside the field owing to the very strong converging action in the region in which the electron-velocity is low. As will be explained later, when V_2/V_1 approaches zero the number of cross-overs inside the field increases, since the converging portion of the mirror becomes stronger and stronger. The experiments to follow are considerably easier to interpret when reference is made to the equipotential surfaces of the system.

Epstein⁽⁸⁾ has applied the usual optical laws to determine the principal planes and focal lengths of electron lenses. Similar experiments have been carried out in this laboratory, and it was with a view to determining these constants for the electron mirror that the following experiments were made. For such a determination it is necessary to know at least two magnifications and the corresponding distances of object and image for a given focusing system. Hence, in order to cover a large range of voltage ratios, the distances of object and image must be variable over a large range. Figure 2 shows diagrammatically the system used. The lens formed between the first two cylinders at potentials V_0 and V_1 produces a real inverted image of A at B when the third cylinder is also at potential V_1 . When the third cylinder is maintained at potential V_2 (negative with respect to the cathode) the image B becomes the virtual object for the mirror formed between cylinders 2 and 3, which produces the final image at C by reflection. Now for a given value of V_2/V_1 , i.e. a given

reflecting system, two values of p (the distance of the object), q (the distance of the image) and m (the magnification) must be obtained. In order to cover the whole range, curves of p and m against V_2/V_1 are obtained for at least two values of q . The distance p_1 is fixed, and q_1 can be varied by altering V_1/V_0 . Also q_1 can be obtained from the known relations for two equal cylinders, which have previously been obtained. From a knowledge of q_1 the quantity p can be obtained, while the varying position of the image C is observed on a movable screen, thus giving q . The mirror magnification m , which is the size of the image C divided by the size of the image B is obtained from the observed magnification of C/A and the previously known magnification B/A . It must be noted here that limitations in the variation of q (three tube-diameters) for which p could be measured with reasonable accuracy kept the two curves of p against V_2/V_1 so close together that no determination of the focal length and principal planes could be made. The curves of p and m against V_2/V_1 for various values of q are nevertheless given, and are of considerable use in setting up mirror systems. The above method would be satisfactory for an investigation of the mirror over a limited range, but the experiments here described were essentially a preliminary survey of the mirror over the entire range.

§ 3. EXPERIMENTAL ARRANGEMENT

The experimental arrangement for investigating the electron mirror is shown in figure 3. The electrons are supplied by a hot oxide cathode C surrounded by a shield A at cathode potential. The beam of electrons is accelerated by the potential V_0

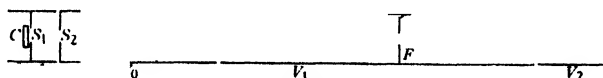


Figure 3.

on the adjacent cylinder and passes through stops S_1 , S_2 and S_3 , and also through a fine-mesh nickel gauze G . An electrostatic lens is produced, between this cylinder and the following one at potential V_1 , which serves the purpose of varying the position of the mirror object. The cylinder at potential V_1 also contains an apertured disc carrying a fluorescent screen F on the side remote from the cathode. This disc is supported from a collar D , sliding on the rod E , by a small wire which passes through a longitudinal slot in the cylinder. The position of the screen can be varied by moving the slider D , by means of an external magnetic field. The image is observed through the electrostatic field of the mirror by means of a telescope T outside the evacuated envelope. A final cylinder V_2 is maintained at a potential negative to the cathode, and it is the field between this cylinder and the preceding one that constitutes the electron mirror. The whole apparatus is aligned accurately and supported inside a glass tube by means of a brass end plate carrying the leads to the electrodes. This is in contact with a ground flange on the tube, and the joint is made vacuum tight with Apiezon sealing compound Q . The other end is closed by a flat glass plate on a ground glass flange and the image is observed through the

plate. The vacuum is maintained by a two-stage mercury diffusion pump backed by a rotary oil pump.

The procedure for observing a reflected image is as follows. The position of the screen F is fixed, giving one value of q , and V_2 is set at some definite potential negative to the cathode, while V_1 is set at a definite potential positive to the cathode. The voltage V_0 is now adjusted until an image of the grid G is obtained on the screen. From the value of V_1/V_0 , and the known object-image relations of the electrostatic lens for this potential ratio, the value of p (figure 2) can be found. Thus p and q are obtained for a given mirror of voltage ratio V_2/V_1 and the overall magnification is obtained by direct measurement, and hence the mirror magnification alone can be obtained. The measurements were repeated for the complete range of values of V_2/V_1 giving p and m as a function of V_2/V_1 for a given q . After this the value of q was changed and a complete series of readings of p and m and V_2/V_1 were obtained for the new value of q .

§4. RESULTS FOR THE ELECTRON MIRROR

Figures 4, 5 and 6 are curves for the various quantities measured. For convenience the position of the zero equipotential surface in terms of percentage of $(V_1 - V_2)$ is given, as well as the voltage ratio V_2/V_1 at which the image is observed.

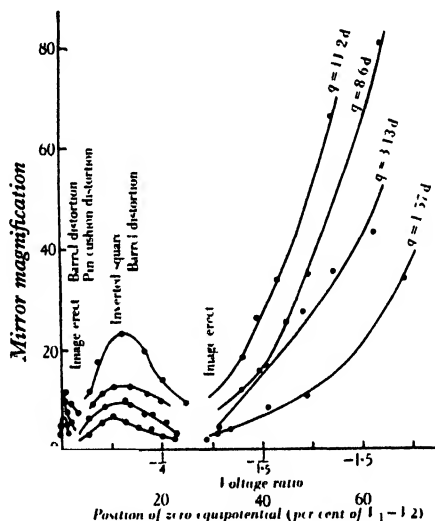


Figure 4. Mirror magnification for various values of q in terms of the tube-diameter d .

Figure 4 shows mirror magnification m as a function of V_2/V_1 for four values of q . For the two higher values of q , corresponding values of p could not be obtained, and hence the values of m for these two curves are only approximate. As in the case of electron lenses the values of q are given in terms of the cylinder diameter, and this is also the case with p in figures 5 and 6. The two graphs in figures 5 and 6 give p as a function of the voltage ratio V_2/V_1 , when $q = 1.57$ tube-diameters and $q = 3.14$ tube-diameters respectively. When the value of V_2/V_1 is between -3 and

$-1/1.5$, the virtual mirror object is quite near the centre of symmetry of the mirror, which probably accounts for the high magnification and high divergence of such a system. As V_2/V_1 decreases to $-1/2.5$, the distance of the mirror object from the centre of the mirror increases to infinity, thus accounting for the decreasing magnification and final cross-over of the beam on the screen. After this first cross-over the mirror object is again near the centre of the mirror, and as V_2/V_1 decreases to $-1/20$, where the second cross-over occurs on the screen, the mirror object again moves off to infinity. This process is repeated as the beam crosses over more and more times, until finally space charge, in the low-velocity region of the mirror, and increased aberrations prevent the formation of a well-defined image.

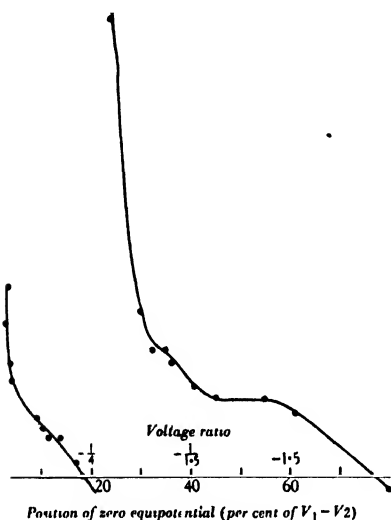


Figure 5. $q = 1.57$ tube-diameters.

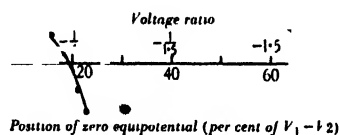


Figure 6. $q = 3.14$ tube-diameters.

The quality of the image was in general very good and its characteristics for various values of V_2/V_1 have been noted in figure 4. For voltage ratios between -4 and -1.5 the image was highly magnified and erect in relation to the virtual object B , figure 2. As V_2/V_1 goes from -1.5 to $-1/2$ the magnification decreases gradually until at about $V_2/V_1 = -1/2$ the system changes from a diverging to a converging one and the image on the screen now becomes inverted in relation to B , and is quite sharp. In the region around $V_2/V_1 = -1/4$ the image of the grid suffers from barrel distortion. On passing to $V_2/V_1 = -1/10$ the image is practically square, and on alteration of V_2/V_1 towards $-1/20$ the image becomes pincushion-shaped. Between $V_2/V_1 = -1/4$ and $V_2/V_1 = -1/24$, the magnification increases to a maximum at $V_2/V_1 = -1/10$ and then decreases. As V_2 continues towards zero a first cross-over is formed in the mirror system at $V_2/V_1 = -1/40$, and one intermediate image is formed, while the image on the screen now becomes erect again and suffers from

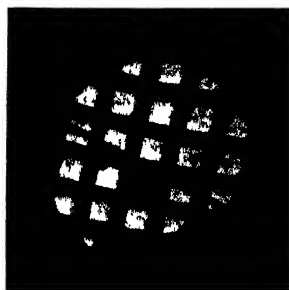
barrel distortion. As V_2/V_1 changes to $-1/100$ the image becomes square and at $-1/200$ it becomes pincushion-shaped. Again, at $V_2/V_1 = -1/400$ a second cross-over is formed in the field and the new image is inverted. This process continues and more and more cross-overs and intermediate images are formed as V_2/V_1 is brought to zero. The images after two cross-overs are, however, very badly distorted. The images of the cross wires tend to converge towards the centre of the field, and as more cross-overs are produced the image becomes unrecognizable and consists merely of bright streamers crossing the centre of the field. The above arrangement did not lend itself to photography of the image owing to the length of the second cylinder and inconvenience occasioned by the movable screen, but photographs were obtained with other two-cylinder systems which behaved in a similar manner. Figure 7 shows at A, B and C the image obtained for three different voltage ratios for a mirror system consisting of a cylinder $1\frac{1}{2}$ in. in diameter followed by a $\frac{1}{2}$ -in. cylinder. The distance q in this arrangement was two tube-diameters. The object was a nickel gauze with a metallized quartz fibre across it. The aperture through which the electrons passed into the mirror can be observed on all the photographs. The magnification of the system was approximately 40. Figure 7 A shows the image obtained at a voltage ratio V_2/V_1 equal to $-1/2.7$, while in B, $V_2/V_1 = -1/17.2$ and in C, $V_2/V_1 = -1/38.4$. As can be seen, the images are very sharp and clear.

Figure 8 illustrates the change in the shape of the image in the region between $V_2/V_1 = -1/200$ for the case of two equal cylinders of diameter $1\frac{1}{2}$ in. A shows slight barrel distortion at $V_2/V_1 = -1/66.6$. B shows a practically square image at an intermediate ratio of $-1/100$, and C shows an image suffering from pincushion distortion at $V_2/V_1 = -1/182$. This change in the character of the image is typical of two-cylinder mirrors when they are behaving as convergent systems, and the cycle is repeated each time a cross-over is produced inside the field of the cylinders. Thus the photographs A, B and C of figure 8 are also representative of the images obtained between voltage ratios of $-1/4$ and $-1/20$. These changes are brought about by the variation in the curvature of the reflecting equipotential surface produced by altering V_2/V_1 , and also by the fact that the electron beam only passes through a selected portion of the field. Both of these effects are peculiar to electron mirrors and cannot be reproduced in lenses.

An interesting example of multiple reflections between the electron mirror and the zero equipotential surface near the cathode is shown in figure 9 A. Five separate images are visible on the screen. One of these images is formed each time electrons pass through the gauze towards the electron mirror and are reflected. A portion of the beam forming the first image from the mirror returns through the hole in the fluorescent screen to the cathode where it is reflected back to the mirror, which produces a second image of the gauze on the screen. Again part of the electron beam passes through to the cathode and, returning, produces a third image. This process continues and more images are formed, but the intensity steadily decreases owing to the fact that a large fraction of the beam is intercepted at the apertures for each reflection. As can be seen in the photograph, the images obtained are not superimposed; this is due to slight misalignment of the system. The superimposition of



A
 $V_2/V_1 = -1/27$

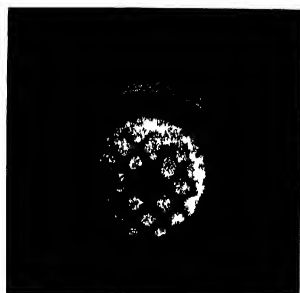


B
 $V_2/V_1 = -1/172$



C
 $V_2/V_1 = -1/384$

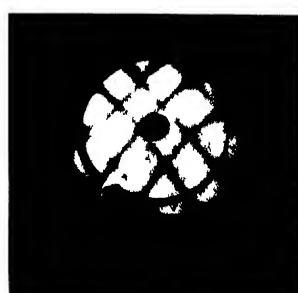
Figure 7.



A
 $I/I_1 = 1/666$



B
 $V_2/V_1 = -1/100$



C
 $V_2/V_1 = -1/182$

Figure 8



A
 $V_2/V_1 = -1/35$



B
 $V_2/V_1 = -1/1$

Figure 9.

these multiple images is really an extremely critical test of alignment, and is similar to the optical method of testing compound lenses for alignment by means of reflections from the individual lens surfaces. The field and space-charge conditions of the cathode for multiple reflections are rather critical, and in the case described the cathode heater was reduced from 4 to 2.5 v. while the aperture S_1 and the cathode screen A were maintained at +9 v. The ratio V_2/V_1 was -1.35 and the mirror consisted of a $1\frac{1}{2}$ -in. cylinder followed by a 1-in. cylinder. The result is undoubtedly dependent also on the cathode spacing behind the aperture S_1 . In this case it was 0.3 mm. for an aperture of diameter 2 mm. The multiple reflections did not occur under the conditions for obtaining single reflections. Figure 9 B shows an image produced by a single reflection with the same two cylinders, but with the cathode screen at the same potential as the cathode and the cathode operating under space-charge conditions. As can be seen, there is no interference due to multiple reflections. The magnification is about 40 times.

§ 5. BEHAVIOUR OF TWO-CYLINDER LENSES AT HIGH VOLTAGE RATIOS

The formation of intermediate images within the field of the system as described for electron mirrors has also been observed in the case of lenses of the accelerating type. The experimental arrangement was the same as in figure 3 for the mirror, but the sliding fluorescent screen F was removed and another one was placed to the right of the final cylinder. The first and second cylinders of potentials V_0 and V_1 respectively were connected together and maintained at V_1 . With this arrangement images could be obtained on the fluorescent screen at very high ratios V_2/V_1 , of the order of 1000. They were distinct, but not of the quality of those obtained at low ratios V_2/V_1 , although they appeared to have less pincushion distortion. It was impossible to make measurements of the focal lengths or of the intermediate image positions, but the general behaviour of the system was quite clear. Figure 10 A is an illustration of the focusing action of the electrostatic field between two cylinders at potentials V_1 and V_2 where V_2/V_1 is small (about 10 to 20) and the focusing is of the well known type. The lens is really compound, and is formed of a converging lens on the left and a diverging lens on the right. The converging portion of the field, however, is at the lower potential, and hence although the field is symmetrical, the converging half is stronger than the diverging half and the result is a converging system. Figure 10 B shows the same two cylinders with V_2/V_1 very large, of the order of 1000. Again point A is reproduced at B , but an intermediate image is also formed at C and the beam crosses over inside the lens. In this case the converging portion of the lens is so strong that the beam crosses over inside the converging field, thus producing an intermediate image. There is, however, still sufficient converging field remaining to reproduce the intermediate image at the point B . Figure 10 C shows the similar behaviour of a decelerating lens when V_2/V_1 is very small, of the order of 0.001. This effect cannot in general be observed in decelerating lenses because of the very low voltage of the final beam, but it must nevertheless occur. In this case of course the converging portion of the lens is in

the second cylinder, which is now at the lower potential. If the voltage ratio V_2/V_1 of the two cylinders of figure 10 B is increased far beyond the value which gives one cross-over and one intermediate image, then we should expect to obtain a second cross-over and a second intermediate image. Similarly for the decelerating lens of figure 10 C we should expect to find a second cross-over and a second intermediate image when V_2/V_1 is made very much smaller. In both cases further cross-overs

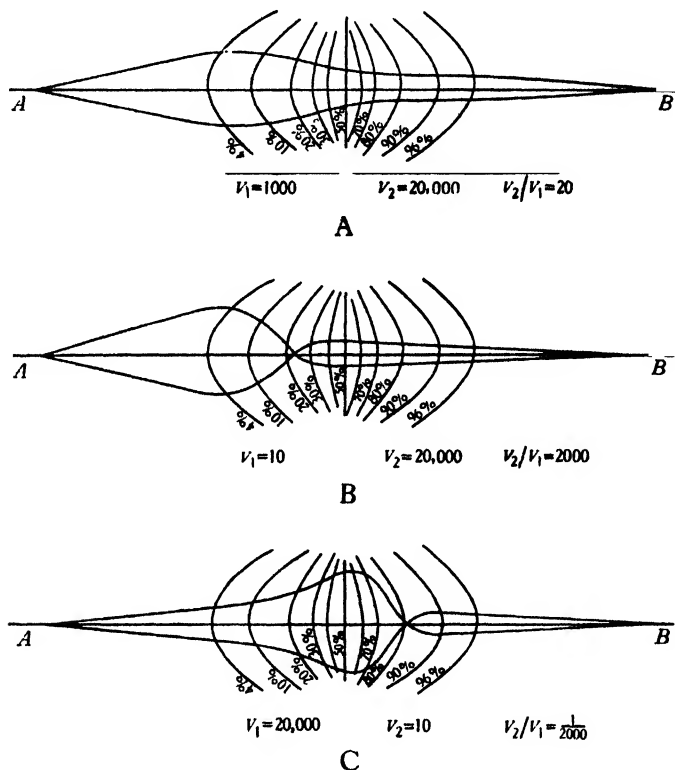


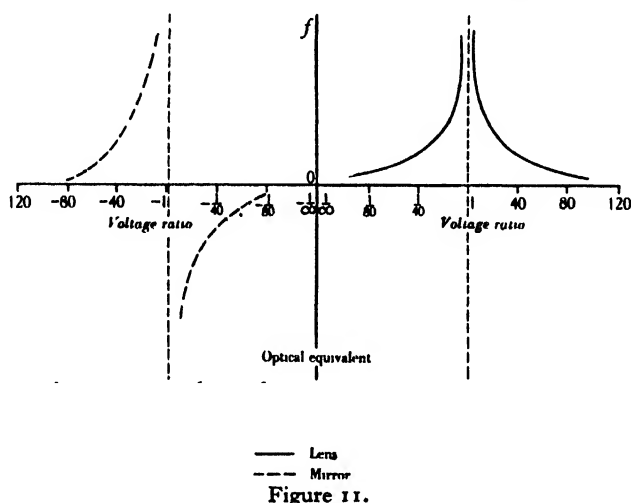
Figure 10.

and intermediate images are to be expected as the converging field is made stronger and stronger. This behaviour is very similar to the formation of intermediate images and cross-overs in magnetic lenses with very high fields.

§ 6. GENERAL PROPERTIES OF THE TWO-CYLINDER FOCUSING SYSTEM

With the additional information which has now been obtained we can completely describe the behaviour of a two-cylinder focusing system with its corresponding optical equivalent. Figure 11 shows qualitatively the results from $V_2/V_1 = -\infty$ to $V_1/V_2 = +\infty$, while below are given the optical equivalents. As V_2/V_1 varies from $-\infty$ to zero, the mirror is at first very strongly divergent. As -1 is approached the system becomes less and less divergent until V_2/V_1 is approximately $-1/3$, when it

changes over and the system becomes convergent in behaviour. From here until $V_2/V_1 = 0$ the convergent portion of the field becomes stronger and stronger, with the result that when V_2/V_1 is about $-1/40$ the first cross-over occurs inside the field and one intermediate image is formed. Again when $V_2/V_1 = -1/400$ a second cross-over occurs and a second intermediate image is formed. The number of cross-overs and intermediate images will continue to increase indefinitely as zero is approached. When $V_2/V_1 = 0$ the system also changes over from a mirror to a converging decelerating system. As in the case of the mirror, the beam crosses over a large number of times when V_2/V_1 is near 0, while as V_2/V_1 increases towards 1 the number of cross-overs and intermediate images decreases and finally the lens behaves as a simple thick lens with no intermediate image. When $V_2/V_1 = 1$ the



focal length of the lens is infinite, and it neither accelerates nor decelerates the electron beam. As V_2/V_1 increases no cross-overs occur inside the system and the latter is a simple convergent accelerating lens, but somewhere in the neighbourhood of $V_2/V_1 = 1000$ the first cross-over occurs and one intermediate image is formed within the lens. For still higher values of V_2/V_1 the number of cross-overs and intermediate images will increase indefinitely as V_2/V_1 approaches infinity. The scale of figure 11 was so chosen that it was impossible to include very high voltage ratios. However, as is shown in the figure, at a voltage ratio of about 100 a parallel beam crosses over inside the lens, but it is not until much higher ratios are reached that divergent beams cross over and intermediate images are formed.

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THE ANALOGY BETWEEN THE PHOTON AND THE ELECTRON AND THE DERIVATION OF THE QUANTUM EQUATION

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ABSTRACT. On the view that the theory of the electron is exactly analogous to the theory of the photon, a quantum law is derived which is shown to require the existence of the first-order equation of the quantum theory. The notation required for this purpose is developed, and it is shown to have certain advantages. The limiting character of the fundamental lengths \hbar/m_0c and e^2/m_0c^2 follows naturally, and the notation suggests that the latter should be regarded as a limit to the application of present physical theory.

§ 1. INTRODUCTION

IN the theory of relativity the path of a photon is described by a null geodesic in four dimensions, and associated with this path is the well known equation of the light wave. This association of a null geodesic and a wave equation is the expression of the wave and particle character of this particular phenomenon. This double aspect, which is now recognized generally in the quantum theory, was first recognized in the case of the photon.

The equation of motion of a particle under gravitational forces according to the theory of relativity is a geodesic, but it is not a null geodesic, while the equation of an electrically charged particle is not a geodesic at all.

The attempt to widen the theory of relativity in order to make the equation of a charged particle in a gravitational and electromagnetic field also a geodesic was made by Kaluza⁽¹⁾ nearly twenty years ago. He found that it was impossible to succeed in this attempt so long as the continuum was of four dimensions only. It was necessary to make use of a continuum of five dimensions, and this discovery indicates that a charged particle such as the electron requires five coordinates for its description. The usual space and time coordinates require to be completed by a fifth which we shall denote by x^5 , placing the affix above the symbol to denote its contravariant character.

The difficulty of interpretation of this fifth coordinate was originally a drawback to the theory proposed by Kaluza. But this difficulty is removed when we recognize x^5 as a cyclic co-ordinate comparable with such a co-ordinate as θ in orbital motion. Such co-ordinates do not appear explicitly in the expression for the energy in the dynamics of systems and x^5 does not appear explicitly in the quantities required for the description of the motion of the electron.

With the advent of the quantum theory Klein⁽²⁾ recognized that the notation

of Kaluza had great advantages for the description of quantum relations. In this case x^5 preserved its character as a cyclic co-ordinate for it was disregarded except in the operation $\partial/\partial x^5$ which was placed equivalent to multiplication by $2\pi im_0 c/h$, where m_0 denotes the rest mass of the electron. This may be interpreted by supposing that the functions containing the fifth co-ordinate do so in the factor

$$\exp \left[\frac{2\pi im_0 c}{h} x^5 \right].$$

In this case again the failure to recognize the character of x^5 was a disadvantage and we are left with little more than a convenient mode of description. But already certain advantages appear. Thus the principle of conservation of momentum generalized in the five-dimensional sense includes the three principles of conservation of mechanical momentum, of energy and of electric charge. In the same way that the theory of relativity unites the first two of these principles, the notation of Kaluza and Klein unites them all.

This notation was used in order to try to show the relation of the quantum theory to the theories of gravitation and of electromagnetism and a very striking discovery was made by J. W. Fisher⁽³⁾, who showed that the path of the electron could be described as a null geodesic in five dimensions. This brings out the wave and particle aspect of the electron and makes it analogous to the photon. It suggests that the electron can be described by a set of field equations like those of the electromagnetic theory of light. This suggestion has been followed successfully and leads to the first-order equation of the quantum theory. These equations were discovered by Dirac who followed a different line of thought and we shall see later on the relation of Dirac's method to the theory now under discussion.

A more recent and very suggestive discovery is that the theory contains the principle of quantization of electric charge⁽⁴⁾. This has brought out the character of x^5 as a cyclic co-ordinate associated with a constant momentum component Π_5 , which must be a multiple of $m_0 c$, where m_0 is a constant recognized as the mass of the electron. Since Π_5 is proportional to the charge associated with the particle we deduce that the charge is a multiple of $\alpha m_0 c^2$, αc being the constant of proportionality between Π_5 and the charge. The constant α is a new constant introduced by Kaluza, which the present theory interprets as $e/m_0 c^2$, e being the charge of the electron.

In the investigation of the relation of the quantum theory to the theory of relativity use was made of the idea of the parallel displacement of a vector, first introduced by Weyl. Eddington showed that Weyl's idea was capable of generalization and this was applied in the present application. But the extent of the generalization required was very slight. It was found that the quantum theory required a system of gauging such that in all displacements, which may be associated with displacements in physics, the change of length of a vector when it undergoes a parallel displacement is zero⁽⁵⁾. This view of the nature of the natural gauge makes the principle of parallel displacement a physical one and not merely a cataloguing device as it was in the theory of Weyl.

This attempt at union of the quantum theory and other branches of physics has led to the recognition of the limitation of the theory, for it has shown that we shall get into difficulty in our space-time description in physics when we attempt to discuss problems in which lengths occur less than αe , that is to say, less than $e^2/m_0 c^2$.

We can compare this with the discovery of the limiting character of the velocity of light which resulted from the attempt to unite, by means of Lorentz's conception of the force on an electric charge, the theories of mechanics and electromagnetism, and also with the discovery of the new constant h and its limiting character which resulted from the attempt to unite the theory of radiation with the classical theory.

The close analogy revealed between the photon and the electron in this way has its counterpart in the quantum theory. As an illustration of this we have only to translate the quantum condition which leads to the quantization of electric charge into the language of matrix operators.

Suppose that we have a total charge q , consisting of n charges e . In this case the total momentum Π_5 is represented by $q/\alpha c$ and the integral relation is⁽⁴⁾

$$\int \Pi_5 dx^5 = n\hbar \quad \text{.....(1).}$$

The matrix form of this is

$$\Pi_5 x^5 - x^5 \Pi_5 = \frac{\hbar}{2\pi i} \quad \text{.....(2).}$$

Π_5 and x^5 are now operators. We write $\Pi_5 = Ne/\alpha c$, where N is an operator with proper values 0, 1, 2, etc., and, instead of x^5 , which has a periodicity $\hbar/m_0 c$, we introduce ω , which has unit periodicity, where $\frac{\hbar}{m_0 c} \omega = x^5$.

Thus the relation becomes

$$N\omega - \omega N = \frac{1}{2\pi i} \quad \text{.....(3),}$$

and is recognized as a well known relation of the quantum theory. It is the custom, since ω is not observed, to replace the equation by another which can be deduced from it, namely,

$$Ne^{2\pi i \omega} - e^{2\pi i \omega} N = e^{2\pi i \omega} \quad \text{.....(4),}$$

or by

$$e^{-2\pi i \omega} N - N e^{-2\pi i \omega} = e^{-2\pi i \omega} \quad \text{.....(5).}$$

A similar equation occurs in the quantum theory of the oscillator which forms the basis of the quantum theory of radiation.

The above equations thus show the close analogy existing between the quantum theory of systems of oscillators and systems of electrons and thus the analogy between the quantum theory of radiation and the quantum theory of electrons. A well known example in which this analogy has been worked out is in Fermi's theory of the beta-ray spectrum.

Our present purpose is to follow up the analogy in the case of the first-order equations of the quantum theory of the electron in the form discovered by Dirac. We shall discuss the nature of the fundamental matrices and introduce Dirac's

equation in a simplified form. It will be found that the limitation to present quantum theory, which has been mentioned, is revealed very simply and its nature and source is explained.

§ 2. THE LINE ELEMENT OF THE FIVE-DIMENSIONAL CONTINUUM

The suggestion made by Kaluza in order to express the track of an electron as a geodesic is that the line element $d\sigma$ should be of a form such that

$$d\sigma^2 = \gamma_{\mu\nu} dx^\mu dx^\nu \quad \dots\dots(6).$$

Summation over μ and ν is to be made for the values 1 to 5. We begin with a statement of the values of the contravariant components $\gamma^{\mu\nu}$, since they have the most direct relation to the components g^{mn} in the theory of relativity.

The Latin affixes m and n may have the values 1 to 4. The relations are

$$\gamma^{mn} = g^{mn}, \quad \gamma^{m5} = -\alpha\phi^m, \quad \gamma^{55} = \alpha^2\phi_m\phi^m + \frac{1}{\gamma_{55}} \quad \dots\dots(7).$$

The quantities, ϕ^m , denote components of the electromagnetic vector potential. The constant α is a new constant in the theory and has been interpreted in the way we have already described. In order to express the track of the electron in the form of a null geodesic we take $\gamma_{55} = 1$, $\alpha = e/m_0 c^2$.

It will be noted that for a null geodesic we can, without loss of generality divide throughout by γ_{55} in the expression (6) and by writing $\gamma_{55} = 1$ we are merely taking the expression with a positive sign before $(dx^5)^2$ for convenience.

In association with equation (7) we have the following values for the covariant components $\gamma_{\mu\nu}$:

$$\gamma_{mn} = g_{mn} + \gamma_{55}\alpha^2\phi_m\phi_n, \quad \gamma_{m5} = \gamma_{55}\alpha\phi_m \quad \dots\dots(8).$$

It will be noted that we can write $d\sigma^2$ in the form

$$d\sigma^2 = g_{mn} dx^m dx^n + \frac{1}{\gamma_{55}} (\gamma_{\mu 5} dx^\mu)^2 \quad \dots\dots(9).$$

This is very convenient for the examination of the relation of this continuum to that of the theory of relativity since the first term is the element ds^2 or $-c^2 d\tau^2$ of that theory, where $d\tau$ denotes an element of the proper time.

We shall write

$$\sqrt{\gamma_{55}} d\theta = \gamma_{\mu 5} dx^\mu \quad \dots\dots(10),$$

so that equation (9) becomes

$$d\sigma^2 = ds^2 + d\theta^2 \quad \dots\dots(11).$$

In the case of a null geodesic $d\sigma^2 = 0$ and $d\theta = c d\tau$. From equation (9) it is evident that ds and $d\theta$ may be regarded as two perpendicular components of $d\sigma$.

The same process can be applied to any vector C with components C^μ . We can write

$$C^2 = g_{mn} C^m C^n + \frac{1}{\gamma_{55}} (\gamma_{\mu 5} C^\mu)^2 \quad \dots\dots(12).$$

This vector may be regarded as made up of a four-dimensional vector with components $A^m = C^m$, and of a component $(\gamma_{\mu 5}/\sqrt{\gamma_{55}}) C^\mu$ normal to the four vector.

We shall describe the latter as A_0 , so that with A^3 equal to $g_{mn} A^m A^n$ we have

$$C^2 = A^2 + A_0^2.$$

When such quantities as the five vector C occur in physics it is the custom to disregard their five-dimensional character and to make use of A and A_0 . This leads to some inconvenience and to a loss of elegance in the notation.

It is important to avoid confusion and, although C and A together with A_0 denote the same quantity, we use a different symbol to lay stress on the fact that C is a five vector while A is a four vector.

By definition $A^m = C^m$ but $A_0 \neq C^5$.

§ 3. RELATION BETWEEN COVARIANT COMPONENTS

Any component C_μ of the covariant five vector is defined to be

$$C_\mu = \gamma_{\mu\nu} C^\nu,$$

and for the four vector we have

$$A_m = g_{mn} A^n.$$

We have

$$A_0 = \frac{\gamma_{\mu 5}}{\sqrt{\gamma_{55}}} C^\mu = \sqrt{\gamma_{55}} (\alpha \phi_m A^m + C^5) \text{ by equation (8)} \quad \dots\dots(13),$$

$$\begin{aligned} C_m &= \gamma_{m\nu} C^\nu = \gamma_{mn} C^n + \gamma_{m5} C^5 \\ &= g_{mn} A^n + \gamma_{55} \alpha \phi_m (\alpha \phi_n C^n + C^5) \text{ by equation (8)} \\ &= A_m + \sqrt{\gamma_{55}} \alpha \phi_m A_0 \end{aligned} \quad \dots\dots(14),$$

$$\begin{aligned} C_5 &= \gamma_{5\mu} C^\mu = \gamma_{5m} C^m + \gamma_{55} C^5 \\ &= \sqrt{\gamma_{55}} A_0 \end{aligned} \quad \dots\dots(15).$$

The element $d\theta$ already introduced is a particular case of A_0 ,

$$d\theta = \sqrt{\gamma_{55}} (\alpha \phi_m dx^m + dx^5).$$

§ 4. THE MATRIX LINE ELEMENT

In order to make use of geometric ideas and of a geometric mode of description in quantum mechanics it has been found convenient to introduce the matrix line element. This is defined to be⁽⁶⁾

$$d\sigma = \gamma_\mu dx^\mu \quad \dots\dots(16),$$

where γ_μ is one of five matrices regarded as of fundamental significance. Associated with them there are contravariant matrices γ^μ and we connect them by means of the same relation as that which holds for vectors,

$$\gamma_\mu = \gamma_{\mu\nu} \gamma^\nu.$$

We also make use of certain relations introduced by Tetrode originally for four-dimensional matrices. These are

$$\gamma_\mu \gamma_\nu + \gamma_\nu \gamma_\mu = 2\gamma_{\mu\nu} \quad \dots\dots(17),$$

and

$$\gamma^\mu \gamma^\nu + \gamma^\nu \gamma^\mu = 2\gamma^{\mu\nu} \quad \dots\dots(18).$$

The latter gives for the cases where μ and ν are not equal to 5

$$\gamma^m \gamma^n + \gamma^n \gamma^m = 2\gamma^{mn} = 2g^{mn} \quad \dots\dots(19).$$

§ 5. THE MATRICES OF THE QUANTUM THEORY⁽⁷⁾

In the quantum theory four matrices α^m together with a fifth β are introduced. We shall now describe β by the symbol α_0 . According to Tetrode these satisfy the relations

$$\left. \begin{aligned} \alpha^m \alpha^n + \alpha^n \alpha^m &= 2g^{mn} \\ \alpha_m \alpha_n + \alpha_n \alpha_m &= 2g_{mn} \end{aligned} \right\} \dots\dots(20).$$

In the notation we have used for the line element g^{11} , g^{22} and g^{33} are all +1 in the case when the gravitational field is neglected. This means that the matrices used by Dirac are equal to these α 's.

In addition we have the relations

$$\alpha_0 \alpha_m + \alpha_m \alpha_0 = 0 \dots\dots(21),$$

$$(\alpha_0)^2 = 1 \dots\dots(22).$$

We shall show that the matrices α^m and α_0 bear the same relation to the matrices γ^μ as the components A^m and A_0 bear to C^μ . We have to show that the α matrices derived from the γ matrices according to the following equations, satisfy equations (20), (21) and (22),

$$\alpha_0 = \sqrt{\gamma_{55}} (\alpha \phi_m \gamma^m + \gamma^5) \dots\dots(23),$$

$$\gamma_m = \alpha_m + \sqrt{\gamma_{55}} \alpha \phi_m \alpha_0 \dots\dots(24),$$

$$\gamma_5 = \sqrt{\gamma_{55}} \alpha_0 \dots\dots(25).$$

The identification of γ^m with α^m causes the first equation (20) to follow at once as a consequence of equation (19) and the definition of α_m as $g_{mn} \alpha^n$ means that Tetrode's second relation (20) is satisfied.

In order to verify equation (21) we note that

$$\alpha_m \alpha_0 = g_{mn} \gamma^n \sqrt{\gamma_{55}} (\alpha \phi_l \gamma^l + \gamma^5) = \sqrt{\gamma_{55}} (\alpha g_{mn} \phi_l \gamma^n \gamma^l + g_{mn} \gamma^n \gamma^5).$$

Thus
$$\alpha_m \alpha_0 + \alpha_0 \alpha_m = 2 \sqrt{\gamma_{55}} (\alpha g_{mn} \phi_l g^{nl} - \alpha g_{mn} \phi^n) = 0.$$

Finally from equation (25)
$$(\gamma_5)^2 = \gamma_{55} \alpha_0^2.$$

But since $(\gamma_5)^2 = \gamma_{55}$ it follows that $\alpha_0^2 = 1$.

The matrix line element may now be expressed in the form

$$d\sigma = \alpha_m dx^m + \alpha_0 d\theta \dots\dots(26),$$

and corresponding to any vector A we have a vector matrix $(\alpha_m A^m + \alpha_0 A_0)$. It is evident that the square of the vector matrix is equal to the square of the vector.

§ 6. THE QUANTUM EQUATION⁽⁸⁾

In the theory of general relativity the law of gravitation is expressed by a relation between the components g_{mn} . The law is arrived at by means of the Riemann Christoffel tensor B^p_{lmn} . The vanishing of this quantity indicates that the geometry of space-time is Galilean, and a law such as $B^p_{lmn} = 0$ is too stringent for the physical world. The law adopted by Einstein is one affecting the contracted tensor G_{lm} , equal to B^p_{lmn} . Originally the law was $G_{lm} = 0$ but later a modification $G_{lm} = \lambda g_{lm}$ was adopted.

It may be expected that a relation of a similar character exists between the fundamental matrices, and it has been shown that the quantum equation of an electron in an electromagnetic field is actually this relation. The form taken by the relation in terms of the matrices γ^μ is simpler and its derivation easier than is the case in which the matrices α^m and α_0 are used. In order to derive the relation we shall make use of Weyl's conception of gauging and apply it to the matrix length. It will be remembered that Weyl modified the scheme of Riemannian geometry by supposing that when a vector was subjected to a parallel displacement it incurred a change in length. His object was to introduce the electromagnetic vector potential into a system of geometry and metrics and so to bring the theory of electromagnetism into the scheme of relativity.

This union is achieved in five-dimensional theory by the use of the coefficients $\gamma_{\mu\nu}$ with the values (7) and (8). We may therefore suppose that no such change of length occurs when a five-dimensional vector with components C^μ undergoes a parallel displacement in the five-dimensional continuum. It may be, however, that the corresponding four-dimensional vector A^m , related as we have seen above to the five-dimensional vector, does undergo a change of length.

We are therefore led to assume that the rule for the change in a vector component when it is displaced in this way is

$$dC^\mu = -\Gamma_{\lambda\nu}^\mu C^\lambda dx^\nu \quad \dots\dots(27),$$

or in terms of the covariant component

$$dC_\mu = \Gamma_{\mu\nu}^\lambda C_\lambda dx^\nu \quad \dots\dots(28),$$

where the Γ 's denote components of the Christoffel bracket expression. This means that the length C^2 , equal to $C^\mu C_\mu$, is unchanged when this displacement occurs.

We shall now investigate the change in the matrix length $\gamma^\mu C_\mu$ when C is so displaced and in order to do this we shall suppose that a matrix ψ exists as a function of the co-ordinates such that⁽⁶⁾

$$L = \gamma^\mu C_\mu \psi \quad \dots\dots(29)$$

remains unchanged when C_μ is changed according to equation (28). ψ is taken to be a matrix with one column only, i.e. there are four components ψ_{11} , ψ_{21} , ψ_{31} and ψ_{41} , which we can conveniently describe as ψ_1 , ψ_2 , ψ_3 and ψ_4 .

The change in L is

$$\frac{\partial \gamma^\mu}{\partial x^\nu} C_\mu \psi dx^\nu + \gamma^\mu \Gamma_{\mu\nu}^\lambda C_\lambda \psi dx^\nu + \gamma^\mu C_\mu \frac{\partial \psi}{\partial x^\nu} dx^\nu = 0 \quad \dots\dots(30).$$

If this is to be true for all displacements and for all vectors, we require

$$\left(\frac{\partial \gamma^\mu}{\partial x^\nu} + \gamma^\rho \Gamma_{\rho\nu}^\mu \right) \psi + \gamma^\mu \frac{\partial \psi}{\partial x^\nu} = 0 \quad \dots\dots(31).$$

We write this in the form⁽⁹⁾

$$\gamma^\mu \frac{\partial \psi}{\partial x^\nu} + K_\nu^\mu \psi = 0 \quad \dots\dots(32),$$

$$K_\nu^\mu = \frac{\partial \gamma^\mu}{\partial x^\nu} + \gamma^\rho \Gamma_{\rho\nu}^\mu \quad \dots\dots(33).$$

We now suppose that a law exists, which we may call the quantum law, affecting $K_\nu{}^\mu$. But there is nothing to suggest the simple law $K_\nu{}^\mu = 0$, in fact this would require ψ to be constant. This appears to be too stringent a condition for our purpose. Thus as in the case with the Riemann-Christoffel tensor we take the less stringent condition

$$K_\mu{}^\mu = 0 \quad \dots\dots(34).$$

Summation over the five values of μ is, of course, implied. This is the quantum law and leads by equation (32) to

$$\gamma^\mu \frac{\partial \psi}{\partial x^\mu} = 0, \quad \dots\dots(35),$$

which we can describe as a law of gauging since it imposes a condition upon the gauging function ψ .

Equation (35) when expressed in terms of the matrices α^m and α_0 is seen to be Dirac's equation, so that ψ is recognized as the function introduced into the quantum theory of the electron. In order to show that this is the case we shall make use of the conditions we have seen to be necessary in describing the path of the electron as a null geodesic. These are

$$\frac{\partial \psi}{\partial x^5} = \frac{2\pi i m_0 c}{h} \psi,$$

and

$$\alpha = e/m_0 c^2.$$

We have according to our notation

$$\gamma^m = \alpha^m \quad \text{and} \quad \gamma^5 = \alpha_0 - \alpha \phi_m \alpha^m.$$

Thus equation (35) becomes

$$\alpha^m \left(\frac{h}{2\pi i} \frac{\partial}{\partial x^m} - \frac{e}{c} \phi_m \right) \psi + m_0 c \alpha_0 \psi = 0 \quad \dots\dots(36),$$

which is the first-order equation of the quantum theory.

§ 7. THE VALUE OF $K_\nu{}^\mu$

We cannot actually derive the value of $K_\nu{}^\mu$ but we can see the form it takes by means of Tetrode's relations and by means of the identity

$$\frac{\partial \gamma^{\mu\nu}}{\partial x^\sigma} + \Gamma_{\alpha\sigma}{}^\mu \gamma^{\sigma\nu} + \Gamma_{\alpha\sigma}{}^\nu \gamma^{\sigma\mu} = 0.$$

Combining this with equation (18) we obtain

$$(K_\sigma{}^\mu \gamma^\nu + \gamma^\nu K_\sigma{}^\mu) + (K_\sigma{}^\nu \gamma^\mu + \gamma^\mu K_\sigma{}^\nu) = 0.$$

It is clear that if $K_\sigma{}^\mu$ is of the form

$$K_\sigma{}^\mu = \Gamma_\sigma \gamma^\mu - \gamma^\mu \Gamma_\sigma \quad \dots\dots(37),$$

this relation is satisfied identically. Γ_σ is an undetermined matrix. Thus

$$\frac{\partial \gamma^\mu}{\partial x^\nu} + \gamma^\rho \Gamma_{\rho\nu}{}^\mu = \Gamma_\nu \gamma^\mu - \gamma^\mu \Gamma_\nu \quad \dots\dots(38).$$

This may be regarded as defining the operation of differentiation of the matrix γ^μ with respect to x^ν .

In the case of the first four components γ^m or α^m and for differentiation with respect to any variable x^n we have

$$\frac{\partial \alpha^m}{\partial x^n} + \alpha^r \Gamma_{rn}^m + \gamma^5 \Gamma_{5n}^m = \Gamma_n \alpha^m - \alpha^m \Gamma_n \quad \dots\dots(39).$$

It must be remembered that Γ_{rn}^m has to be calculated for the five-dimensional continuum and that it is not equal to the corresponding quantity in four dimensions, viz. $\left\{ \begin{smallmatrix} rn \\ m \end{smallmatrix} \right\}$.

The equation (39) suggests the four-dimensional form

$$\frac{\partial \alpha^m}{\partial x^n} + \left\{ \begin{smallmatrix} rn \\ m \end{smallmatrix} \right\} \alpha^r = \Gamma_n \alpha^m - \alpha^m \Gamma_n \quad \dots\dots(40).$$

Equations (39) and (40) are not identical, but they differ only by a term multiplied by the factor $e/m_0 c^2$, which makes the difference small⁽¹⁰⁾.

It is thus natural to adopt the form (40) for the α^m . When the gravitational field exerts no influence upon the phenomenon considered, as is always the case in quantum problems, equation (40) becomes

$$\frac{\partial \alpha^m}{\partial x^n} = \Gamma_n \alpha^m - \alpha^m \Gamma_n \quad \dots\dots(41).$$

In the particular case when x^n is the fourth co-ordinate ($x^4 = ict$), equation (41) takes the form

$$\frac{\partial \alpha^m}{\partial t} = \frac{2\pi i}{h} (H \alpha^m - \alpha^m H) \quad \dots\dots(42),$$

where $(2\pi i/h) H$ denotes $ic\Gamma_4$.

It will be recognized that this is the equation adopted in the quantum theory for the differentiation of an operator with respect to the time, H being the quantum Hamiltonian operator. The treatment here may be regarded as providing the derivation of this differentiation in the case of the matrix operators α^m .

From equation (42) we adopt the suggestion⁽¹¹⁾ that for any operator Q

$$\frac{dQ}{dt} = \frac{\partial Q}{\partial t} + \frac{2\pi i}{h} (HQ - QH) \quad \dots\dots(43),$$

the partial differentiation with respect to Q being included on the right-hand side since, in the general case, an operator may contain the time explicitly in its components.

§ 8. CHANGE OF LENGTH WITH PARALLEL DISPLACEMENT

The foregoing treatment is based on the assumption that the length of a vector C is unchanged when it undergoes a parallel displacement. But since $C^2 = A^2 + A_0^2$, it does not follow that A undergoes no change when it is subject to a parallel displacement in four dimensions.

It has been deduced from the idea that the quantum equations indicate a modification in Weyl's gauging law that the change of length in A is given by⁽¹²⁾

$$\frac{dA^2}{A^2} = -\frac{2\pi im_0 c}{h} dx^5.$$

Thus the change depends only upon changes in dx^5 .

These considerations have also suggested that dx^5 changes by amounts which are integral multiples of $h/m_0 c$ in those cases which have a physical significance. Thus in the physical world the displacements are such that the change of length is zero. It may be that this is the significance of the cyclic character of x^5 . It follows that a limitation exists in our description of the physical world which is expressed by

$$dx^5 \leq h/m_0 c \quad \dots\dots(44).$$

We do not make use of x^5 explicitly so that we must make use of a substitution provided by

$$d\theta = \sqrt{\gamma_{55}} (\alpha \phi_m dx^m + dx^5) \quad \dots\dots(45).$$

If we apply this to the track of a charge e with $d\theta = c d\tau$ and $\gamma_{55} = 1$, we have

$$dx^5 = c d\tau - \alpha \phi_m dx^m.$$

Thus the limitation (44) becomes

$$c d\tau - \alpha \phi_m dx^m \leq h/m_0 c \quad \dots\dots(46),$$

$$m_0 c^2 d\tau - \frac{e}{c} \phi_m dx^m \leq h.$$

The significance of this has already been discussed⁽¹³⁾. It means that in any case where $(e/c) \phi_m dx^m$ is small, $d\tau \leq h/m_0 c^2$. This condition holds approximately for charges moving in orbits of light atoms where ϕ_1 , ϕ_2 and ϕ_3 are zero and $\phi_4 = Ne/r$, Ne denoting the nuclear charge. In this case the value of r is sufficiently great to cause the second term to be neglected. We deduce that in the orbits no element of time less than $h/m_0 c^2$ is observable⁽¹⁴⁾. But the case is different where two charges e of opposite sign approach one another to a distance of the order of $e^2/m_0 c^2$. Then, supposing for the sake of illustration that the velocities of the charges are well below that of light so that we can regard $d\tau$ as an interval of ordinary time, the formula gives a very large interval for the smallest element of time dt which we can introduce into our equations. For the case of charges approaching one another within this distance our conception of localization in time breaks down. This is the limitation which we mentioned above as resulting from the attempt to study the relation of the quantum theory to the theory of electromagnetism and to the principle of relativity. The result has been to show the limiting character of the length $e^2/m_0 c^2$. It would appear reasonable to conclude that we shall find difficulties in our theory when we attempt to consider lengths of this order of magnitude⁽¹⁵⁾.

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A NOTE ON THE NEAR ULTRA-VIOLET BAND SYSTEM OF SnO

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ABSTRACT. The note refers to Connelly's paper on SnO and Jevons, Bashford and Briscoe's paper on GeO, which appeared in these *Proceedings* in 1933 and 1937 respectively. In the latter it was pointed out that, judged by the data for related band systems of the monoxides of group-IV(*b*) elements, Connelly's values of the anharmonic coefficients $x_e \omega_e$ were anomalous, the value 3.6 cm^{-1} for the ground state being slightly low, and the value 1.1 cm^{-1} for the excited state being much too low. As a result of a re-examination of Connelly's band-head data the expression

$$\nu_{\text{head}} = 29624.9 + (582.6u' - 3.08u'^2 - 0.135u'^3) - (822.4u'' - 3.73u''^2)$$

is now proposed for the $A \rightleftharpoons X$ system, and the anomalies are thereby removed.

SO far as it has been investigated the spectrum of SnO consists of three band systems $B \rightarrow X$, $A \rightleftharpoons X$ and $D \rightarrow X$, which are analogous to the SiS systems $A \leftarrow X$, $B \leftarrow X$ and $C \leftarrow X$ respectively⁽¹⁾, and a few bands attributed to a fourth system $C \rightarrow X$ ⁽²⁾, which appears to have no counterpart in SiS. In every case the bands degrade towards the red. The prominent SnO system $A \rightleftharpoons X$, known in various flame, arc and spark sources for more than half a century, has been observed by Connelly⁽³⁾ both in emission from $\lambda 3071$ to $\lambda 4488$ by a high-voltage a.c. discharge through a flame of hydrogen charged with SnCl_4 vapour, and also in absorption by the flame itself. A recent rotational analysis of three bands of this system by Mahanti and Sen Gupta⁽⁴⁾ indicates an electronic transition $A^1\Sigma \rightleftharpoons X^1\Sigma$. The less extensive systems (or fragments of systems) $B \rightarrow X$ and $C \rightarrow X$ consist of about 20 bands in the region $\lambda 3854$ – $\lambda 4569$, overlapping the visible end of $A \rightleftharpoons X$; * bands of these were recorded, together with $A \rightarrow X$, by the earlier investigators, notably Eder and Valenta and von der Seipen, and have been observed more recently by Mahanti⁽²⁾ in the arc in air, by Connelly in the discharge through flame and by the present writer⁽⁵⁾ in an uncondensed discharge through a mixture of O_2 and SiCl_4 vapour in a discharge tube. The more refrangible system $D \rightarrow X$ was discovered by Loomis and Watson⁽⁶⁾ in the region $\lambda 2390$ – $\lambda 3090$ in a tin arc in oxygen at reduced pressure. It is with the main system $A \rightleftharpoons X$ that this note is concerned.

* Mahanti's⁽²⁾ interpretation of the common lower state of what are now called $A \rightleftharpoons X$ and $B \rightarrow X$ as an excited state of SnO, the lower state of $C \rightarrow X$ being the ground state, was, of course, disproved by Connelly's observation of $A \rightleftharpoons X$ in absorption⁽³⁾, and is implicitly withdrawn in Mahanti and Sen Gupta's recent paper⁽⁴⁾.

In a recent paper in these *Proceedings*⁽⁷⁾ on the ultra-violet system of ⁶⁴GeO, a graphical study was made of the vibrational coefficients of both upper and lower states in the band systems of the monoxides and monosulphides of the group-IV (b) elements which appeared to be analogous to the fourth positive system of CO and the well known ultra-violet systems of CS and SiO. For SnO the extensive system $A \rightleftharpoons X$ was, naturally, chosen for this study and Connelly's expression⁽³⁾,

$$\nu_{\text{head}} = 29626 \cdot 1 + (578 \cdot 9u' - 1 \cdot 1u'^2 - 0 \cdot 32u'^3) - (821 \cdot 9u'' - 3 \cdot 6u''^2)$$

was accepted (u is written here for $v + \frac{1}{2}$). This expression differs considerably, especially in regard to the upper state, from Mahanti's expression for the same system, namely

$$\nu_{\text{head}} = 29630 \cdot 5 + (586 \cdot 0u' - 6 \cdot 0u'^2) - (824 \cdot 0u'' - 4 \cdot 0u''^2),$$

although the assignments of v' and v'' to the bands observed by both are the same in the two cases. The discrepancy is due to the fact that Connelly's observations, extending to $v' = 8$, require a cubic term for the higher levels and also bring to light very large perturbations of rotational levels associated with the vibrational level $v' = 3$, whereas Mahanti's observations, which end with $v' = 3$, neither require a cubic term nor reveal the perturbations.

It was found⁽⁷⁾ that, when the vibrational coefficients ω_e and $x_e\omega_e$ are plotted against the number of electrons in the molecule, two pairs of uninflected curves can be drawn for the ground states of the monoxides and the monosulphides (figure 3 in the GeO paper⁽⁷⁾), and two similar pairs for the excited states (figure 4⁽⁷⁾). In the case of SnO, the first coefficients ω_e'' and ω_e' fall exactly on their respective curves, and the second coefficient $x_e''\omega_e''$ for the ground state ($3 \cdot 6 \text{ cm}^{-1}$) also falls on its curve although it gives the oxide curve a minimum for which there is no counterpart in the corresponding sulphide curve, but Connelly's value ($1 \cdot 1 \text{ cm}^{-1}$) of the second coefficient $x_e'\omega_e'$ for the upper state is much too low to fall on any simple curve passing through the $x_e'\omega_e'$ values for the other monoxides. The difficulty is not to be overcome by discarding Connelly's coefficients in favour of Mahanti's, for, according to the graphs, while Mahanti's value ($4 \cdot 0 \text{ cm}^{-1}$) of $x_e''\omega_e''$ is entirely satisfactory, his value ($6 \cdot 0 \text{ cm}^{-1}$) of $x_e'\omega_e'$ is about as much too large as Connelly's ($1 \cdot 1 \text{ cm}^{-1}$) is too small.

As Connelly's band-head measurements are the more extensive it has been thought desirable to see whether they can be satisfactorily represented by any other expression than that quoted above, the assignments of v' and v'' remaining unchanged. Both the wave-numbers corresponding to the measured wave-lengths in Connelly's table 1 and also the vibrational intervals in his table 2 have been checked.* Those intervals that involve comparatively rough measures of band-heads (shown in parentheses in Connelly's table) have been ignored entirely. The means of the others are as follows:

* For the 7, 2 band either λ or ν is given wrongly. It has been assumed that $\nu 31738 \cdot 3$ is correct and that λ should be $3149 \cdot 86$ instead of $3149 \cdot 16$.

Excited state									
v'	$\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$	$3\frac{1}{2}$	$4\frac{1}{2}$	$5\frac{1}{2}$	$6\frac{1}{2}$	$7\frac{1}{2}$	
$\Delta G' (v')$	575.2	563.6	541.9	583.6	541.1	532.7	517.1	502.9*	
Ground state									
v''	$\frac{1}{2}$	$1\frac{1}{2}$	$2\frac{1}{2}$	$3\frac{1}{2}$	$4\frac{1}{2}$	$5\frac{1}{2}$	$6\frac{1}{2}$	$7\frac{1}{2}$	$8\frac{1}{2}$
$\Delta G'' (v'')$	814.9	806.1†	800.6	793.7	784.7	776.5‡	772.9	764.4	752.4

* $\Delta G' (7\frac{1}{2})$ must be discarded since its value depends entirely on measurements of the 7, 4 and 8, 4 band-heads, and the latter is superposed on the 2, 0.

† Value of $\Delta G'' (1\frac{1}{2})$ obtained after correction of the interval between the 5, 1 and 5, 2 band-heads from 806.3 to 804.3.

‡ Value of $\Delta G'' (5\frac{1}{2})$ obtained after correction of the interval between the 1, 5 and 1, 6 band-heads from 783.1 to 777.1.

These have been used in a graphical determination of the coefficients.

The ground state presents no difficulty whatever. In the excited state, however, the intervals $\Delta G' (1\frac{1}{2})$, $\Delta G' (2\frac{1}{2})$ and $\Delta G' (3\frac{1}{2})$ are affected, as Connelly's figure 3 clearly shows, not only by the very large perturbations at $v' = 3$, but also by smaller perturbations at $v' = 2$ not mentioned by Connelly, and the single observation of $\Delta G' (7\frac{1}{2})$ is not entirely satisfactory. Only the intervals $\Delta G' (\frac{1}{2})$, $\Delta G' (4\frac{1}{2})$, $\Delta G' (5\frac{1}{2})$ and $\Delta G' (6\frac{1}{2})$, therefore, can be used in the derivation of the coefficients of u' , u'^2 and u'^3 .

In the absence of a term in u'^3 the value of

$$\frac{1}{8} \{ \Delta G' (\frac{1}{2}) - \Delta G' (4\frac{1}{2}) \}, \text{ namely } \frac{1}{8} \{ 575.2 - 541.1 \} \text{ or } 4.26 \text{ cm}^{-1},$$

would, of course, be a good estimate of $x_e' \omega_e'$, and as such it would be not much too large in comparison with the values of $x_e' \omega_e'$ for GeO and PbO, namely 4.24 and 2.33 cm^{-1} respectively; it would, indeed, be much better than either Connelly's 1.1 or Mahanti's 6.0. A term in u'^3 is necessary, but it is unlikely to be so large as to reduce $x_e' \omega_e'$ from about 4.26 to 1.1. It is reasonable, then, to seek an expression with a much larger coefficient of u'^2 , and a much smaller one of u'^3 , to represent the unperturbed band-heads. Such an expression has been obtained, namely

$$\nu_{\text{head}} = 29624.9 + (582.6u' - 3.08u'^2 - 0.135u'^3) - (822.4u'' - 3.73u''^3).$$

In view of the fewness and irregularity of the available data no accuracy is claimed for the last figure in any of the coefficients. The residuals ($\nu_{\text{obs.}} - \nu_{\text{calc.}}$) are so small that no importance need be attached to the anomaly presented by Connelly's expression. As ω_e' for this state of SnO, Howell⁽¹⁾ gives 582 cm^{-1} , which is in fair agreement with the value now proposed, but he does not state whence it is obtained, or publish his own SnO absorption data.

In figures 3 and 4 of the GeO paper⁽⁷⁾, the PbO coefficients used were those of Shawhan and Morgan's⁽⁸⁾ expression for the B \rightleftharpoons X system, namely

$$\nu_{\text{head}} = 22889.9 + (496.6u' - 2.33u'^2) - (722.5u'' - 3.75u''^2);$$

unfortunately Howell's expression for the same system⁽¹⁾,

$$\nu_{\text{head}} = 22884.9 + (498.0u' - 2.20u'^2) - (721.8u' - 3.70u''^2),$$

was overlooked. If the latter expression and that now proposed for SnO be

adopted, both $x_e'\omega_e'$ and $x_e''\omega_e''$ diminish from GeO to PbO, just as they do from GeS to PbS⁽⁷⁾, thus:

	GeO	SnO	PbO
$x_e'\omega_e'$	4.24	3.08	2.20
$x_e''\omega_e''$	4.30	3.73	3.70

The SnO value now falls on a smooth $x_e'\omega_e'$ curve (figure 4⁽⁷⁾) and the $x_e''\omega_e''$ curve for the oxides (figure 4⁽⁷⁾) no longer has a minimum at SnO. The slight changes in the coefficients of u' and u'' have no effects on the ω_e' and ω_e'' curves for the oxides.

In a forthcoming paper⁽⁹⁾ on the recently discovered band spectrum of SiS, the reciprocals of the coefficients, instead of the coefficients themselves, are plotted against the number of electrons, in order that graphs of simpler form and smaller curvature may be obtained, and irregularities in the values of the coefficients made more evident. The values now proposed for SnO and PbO are far more satisfactory than those used previously, and it would appear that any further improvement for SnO can only be obtained from entirely new observational data.

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NOTE ON THE USE OF PROBABILITY PAPER

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ABSTRACT. The method of plotting observations on probability paper becomes clear when the curve on probability paper is regarded as an integral of the histogram. The observations are divided into intervals, which may often conveniently be the natural interval of measurement, and the total frequency of observations up to and including the n th interval is plotted against the upper end of the n th interval. It is shown that in drawing a straight line to fit the observations, less weight should be attributed to deviations from the line towards its ends than in the middle regions.

§ 1. INTRODUCTION

DURING the course of an investigation into the nature of the graininess of photographic materials, a considerable amount of data was secured concerning the statistical variation of density over the area of the materials. The time required for the calculation of the mean distribution curve, which was expected to be Gaussian, by the usual methods was considered prohibitive, and recourse was had to probability paper^(1,2). It was found that there was some disagreement concerning the proper use of this method of representing statistical data, and it is the purpose of the present note to put forward what is believed to be the correct method.

Probability paper is printed with a uniform scale of abscissae, but with ordinates so scaled that if the percentage of observations which have values up to a certain figure is plotted as ordinate against that figure as abscissa for a series of values, a straight line can be drawn through the plotted points, when the distribution is Gaussian.

§ 2. AN EXAMPLE

We shall take an example from the investigation mentioned above. Table 1 shows the percentage of occurrences of certain densities in a sample of photographic material. The densities are measured from an arbitrary zero.

The densities were read to 0.001: in other words, it is assumed that a density labelled 0.028 may in fact lie anywhere between 0.0275 and 0.0285. Thus a histogram with 0.001 as the interval may be constructed directly from the observations, as shown in figure 1A. The curve to be obtained on probability paper is then the integral of this histogram, but drawn with suitably distorted ordinates. Therefore, the total percentage of observations up to and including a nominal density of 0.028 should be plotted at 0.0285 and the total percentage recorded up to 0.029 should be plotted at 0.0295, and so on. The only reasonable representation of the course

of the curve joining these two points, or any other similar pair, is a straight line, corresponding with integration of the histogram. Presumably this line should be straight for an integral drawn with a uniform scale of frequency, and therefore curved when drawn on probability paper. However, as the difference is not great the points on probability paper have been joined by straight lines in figure 1 B. It will be noted that the two end points, 0 and 100 per cent, are off at infinity,

Table 1

Density	Frequency (per cent)	Total frequency (per cent)
0.019	0.5	0.5
0.020	0.5	1.0
0.021	0.0	1.0
0.022	1.5	2.5
0.023	0.5	3.0
0.024	3.0	6.0
0.025	4.5	10.5
0.026	5.0	15.5
0.027	4.0	19.5
0.028	8.5	28.0
0.029	7.5	35.5
0.030	12.5	48.0
0.031	9.0	57.0
0.032	8.0	65.0
0.033	5.5	70.5
0.034	6.5	77.0
0.035	11.0	88.0
0.036	3.0	91.0
0.037	2.5	93.5
0.038	2.0	95.5
0.039	1.5	97.0
0.040	2.0	99.0
0.041	0.5	99.5
0.042	0.5	100.0

owing to the nature of the scale of ordinates. It is probably the omission of these points, in their correct places on the scale of abscissae, that has led to the confusion already mentioned concerning the proper method of plotting. If the points are plotted in a way different from that suggested here, it will be found that if in summing the individual frequencies of table 1, for instance, we start from the low-density end of the series of observations, we obtain a curve different from that which we should obtain by summing from the high-density end and using a reversed frequency scale. This is clearly an improper result.

In practice it is hardly necessary to join up the plotted points. It is desirable, however, to plot a point for every interval in the histogram. That is to say, when a value does not appear among the actual observations it should still be plotted, as at *a* in figure 1 B, with the same frequency as the preceding value. Naturally, the histogram is not drawn in practice when probability paper is used. For straight-forward observations the natural interval may conveniently be adopted as in the above example. When the quantities are derived from other observations there may be no natural interval, and the observations should then be classed into intervals exactly as if the histogram were to be drawn.

§ 3. THE STRAIGHT LINE REPRESENTING THE OBSERVATIONS

In estimating the Gaussian distribution which fits an observed distribution it is usual to obtain the constants of the Gaussian distribution by making the first and second moments of the Gaussian distribution equal to the first and second moments of the observed distribution. It will be supposed that the straight line should be drawn so as to fulfil these two conditions. As may readily be seen by reference to figures 1A and 1B, if Δf_n is the deviation of the observed frequency from the

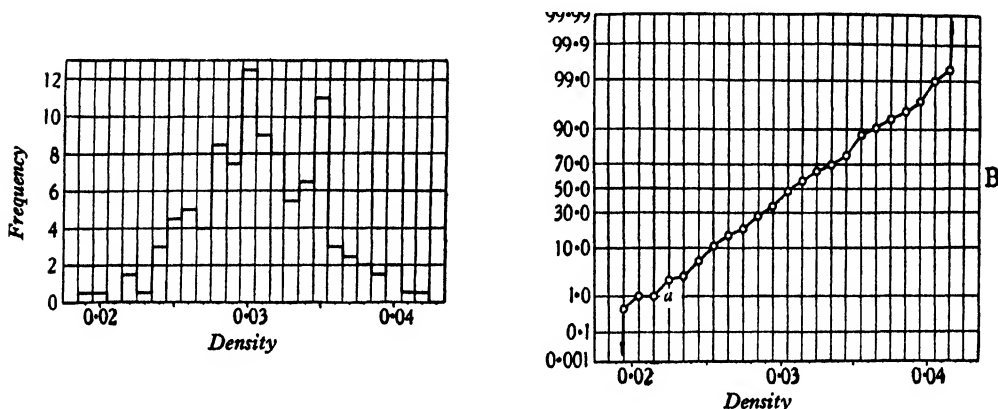


Figure 1. Relation between the histogram A and the curve on probability paper B.

frequency indicated by the straight line at x_n , the point dividing the n th interval from the $(n+1)$ th, equality of the first moments is obtained when*

$$\Sigma \left(\frac{x_n + x_{n+1}}{2} - x_0 \right) (\Delta f_{n+1} - \Delta f_n) = 0$$

and equality of the second moments when

$$\Sigma \left(\frac{x_n + x_{n+1}}{2} - x_0 \right)^2 (\Delta f_{n+1} - \Delta f_n) = 0.$$

These conditions may be reduced, by writing out a few terms and bringing together both terms containing Δf_n , to

$$\Sigma \Delta f_n = 0,$$

and

$$\Sigma \left(\frac{x_{n+1} + 2x_n + x_{n-1}}{4} - x_0 \right) \Delta f_n = 0.$$

If the intervals $x_{n+1} - x_n$ and $x_n - x_{n-1}$ are equal, the last condition becomes

$$\Sigma (x_n - x_0) \Delta f_n = 0.$$

If also Δf_n is small, the ordinate-difference Δy_n , figure 2, between the straight line and f_n , the observed frequency, may be taken as $\Delta f_n / (df/dy)_n$ approximately,

* A slight deviation has been made here from standard practice in the calculation of the moments of the Gaussian distribution, in that the quadrature is approximate.

$(df/dy)_n$ being the value in the neighbourhood of f_n . Moreover the equation to the straight line may be taken as $y = m(x - x_0)$,

and the two conditions to be fulfilled, when written in terms of Δy_n , become

$$\Sigma (df/dy)_n \Delta y_n = 0 \quad \dots\dots(1),$$

$$\Sigma (x_n - x_0) (df/dy)_n \Delta y_n = 0 \quad \dots\dots(2).$$

Both these conditions are fulfilled if

$$\Sigma (df/dy)_n \Delta y_n^2 \quad \dots\dots(3)$$

is a minimum;

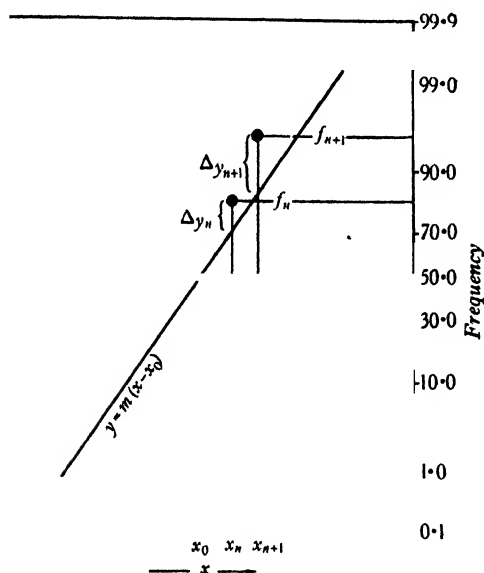


Figure 2. Relation between frequency and ordinate-differences.

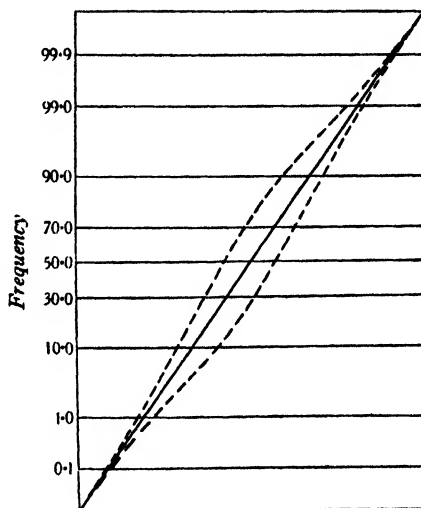


Figure 3. Importance to be attributed to deviations from the straight line at different frequencies.

for on differentiating (3) with respect to x_0 we find that

$$\Sigma 2 (df/dy)_n \Delta y_n (\partial \Delta y_n / \partial x_0) = 0,$$

or, since $\partial \Delta y_n / \partial x_0$ is equal to $-m$,

$$-2m \Sigma (df/dy)_n \Delta y_n = 0,$$

which, except for the constant term $-2m$, is identical with equation (1). Also, differentiating equation (3) with respect to m , we find that

$$2 \Sigma (df/dy)_n \Delta y_n (\partial \Delta y_n / \partial m) = 0$$

or, since

$$\partial \Delta y_n / \partial m = x_n - x_0,$$

$$\Sigma (df/dy)_n (x_n - x_0) \Delta y_n = 0,$$

which is condition (2).

Thus the straight line representing the Gaussian distribution should be drawn

through the plotted points according to the condition (3). Naturally, if this condition is to be fulfilled exactly a considerable amount of computation is involved, and the best thing then is to calculate m and x_0 from the original data by the usual methods of statistics, and to avoid the use of probability paper entirely. But the condition (3) is still useful for indicating the weight to be placed on the individual observations when the best line is being estimated by visual judgement, for it shows that the importance to be placed on the deviation of a point from the straight line is proportional to $\sqrt{(df/dy)}$ in the neighbourhood of the point. In figure 3 this quantity is shown graphically by the ordinate separation between the two broken lines, and indicates that only half the weight should be given to deviations at frequencies of 5 and 95 per cent as compared with that given to deviations at frequencies around 50 per cent. At frequencies of 0.8 and 99.2 per cent the weight should be only one-quarter. With this difference the problem of drawing the best fitting straight line is exactly the same as that of drawing the best line, by visual estimation, for ordinary experimental results for which one might expect a least-squares solution to be the best.

Some difficulty may be felt concerning the end points at 0 and 100 per cent; similar difficulties are not unknown in statistics apart from the use of probability paper. The simplest practical solution is to neglect them entirely in drawing the straight line, on the ground that the straight line through the remaining points would remain substantially unchanged if the number of observations were increased, although the points plotted, apart from those at 0 and 100 per cent, would then reach higher and lower frequencies.

The observations already mentioned confirm the soundness of this method of weighting, for the deviations of the points from the curves are quite obviously greater towards the ends of the lines than in the middle. In fact, the mean deviation from the line has been found to be roughly proportional to the reciprocal of the above weighting factor $\sqrt{(df/dy)}$ for different frequencies.

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THE INTEGRATION OF LARGE NUMBERS OF X-RAY CRYSTAL REFLECTIONS

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Communicated by Dr F. J. Harlow, 23 June 1938. Read in title 14 October 1938

ABSTRACT. The experiments described show that if a positive film is printed from an x-ray negative, the change in the transparency of the former can be made directly proportional, over an extended range, to the intensity of the original x-ray beam. The transmitted light can therefore give the integrated x-ray value of a patch of non-uniform blackening without the necessity of a two-dimensional point-by-point integration. The application of this principle to x-ray analysis of crystal structure is discussed.

§ 1. INTRODUCTION

THE advance of x-ray crystal analysis and in particular of x-ray work on proteins requires the measurement of large numbers of photographically recorded x-ray intensities and a rapid method of measuring them would be welcome. In the present paper it is shown that by making a print of the x-ray film, which will be called the negative, on another film, the positive, the change of transparency of the latter, for a considerable range of intensities, is proportional to the x-ray exposure. This enables the measurement of the film to be completed in about one-tenth of the time required by existing methods and without the use of complicated apparatus such as the alpha-ray photometer⁽¹⁾ or the mechanical integrator⁽²⁾ at present necessary.

It must be remembered throughout the work that the usual linear {density, exposure} characteristic of x-ray films is of no help in this direct method of integrating, because the density is defined as the common logarithm of the reciprocal of the transparency. It is a linear {transparency, exposure} characteristic that is required, because optical photometers measure the light which the film transmits.

§ 2. APPARATUS AND METHOD

The photometer employed is a simple system for focusing a uniform exploring beam on the film. The transmitted light is received by a Weston Photronic cell, the current in which is directly proportional to the intensity of the incident light, so that no calibration is needed. Further, the currents are of sufficient magnitude to eliminate the need for amplification when a galvanometer with a sensitivity of about 100 mm. per μ a. is used. The photocell shows a slight initial drift when exposed to light, unless the light is allowed to diverge sufficiently before striking the photocell. Some of the light which is scattered at a wide angle by the film will

now fall outside the photocell but may with advantage be returned by a cylindrical mirror, such as a tube of aluminium foil. The light-source used in the experiments was a 12-volt 48-watt lamp of the projector type, but for routine work a 12-volt 100-watt lamp would be better. The lamp was operated from a floating accumulator.

The success of this method of integrating depends on the balancing of the characteristics of the negative and positive films to give a resultant linear {transparency, exposure} relation. The characteristic of the negative film was determined by the use of a cam giving a wedge of linear exposure. x-ray radiation from targets of molybdenum and of copper were used; each gave a curve of the same shape, figure 1A and 1B. In agreement with the findings of other workers⁽³⁾ no induction

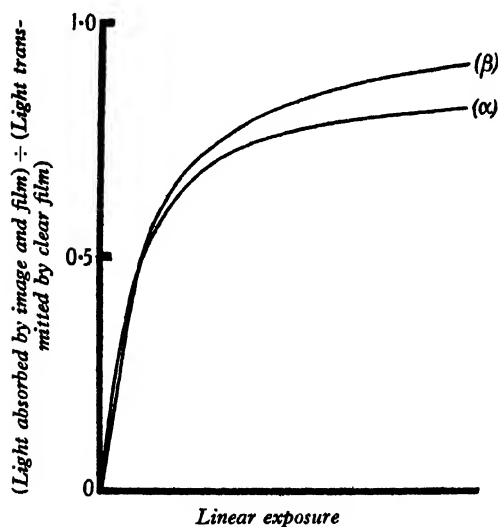


Figure 1A. Curve α : film developed by Agfa Rodinal. Curve β : film developed with the more contrasty x-ray developer.

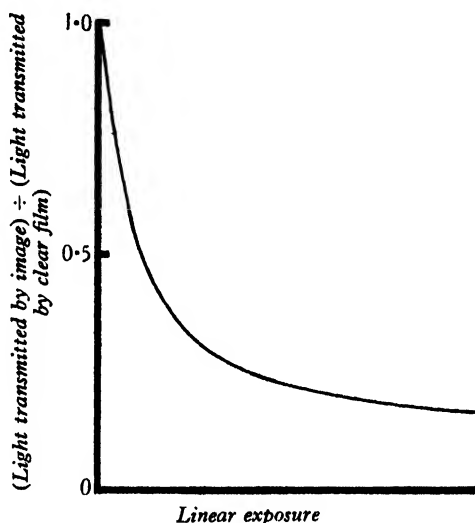


Figure 1B.

period was observed. For our purpose the number of x-ray films from which to choose is extremely limited when compared with the number of optical films available for the positive. Further, on the positive the exposure ranges from a minimum to a maximum, and hence only a portion of the characteristic is used. This portion may be selected from the most favourable part by correct choice of the printing exposure.

The conditions to which the positive emulsion must conform may be found as follows. Let figure 2A represent the characteristic of the negative film, the axes being as in figure 1B. Take points A, B, C, D, \dots at equal intervals along the exposure axis (i.e. along the wedge); the light-intensities for printing on the positive film are then proportional to $AA', BB', CC', DD', \dots$ and we require them to produce on the positive a series of transparencies each of which differs from its neighbour by a constant amount. If we now make OY an exposure axis (it is parallel to the exposures AA', BB', \dots) and OX a transparency axis, then AB ,

BC , ... become the constant differences in the neighbouring transparencies and so we obtain the requirements of the positive characteristic. This curve is redrawn in figure 2B. We note that the scale of the new axes may be chosen at will, and that the zero of the transparency axis lies anywhere on XO produced. It is now only necessary to select an appropriate emulsion and to choose the developer and adjust the printing exposure so as to obtain the best quality in the positive.

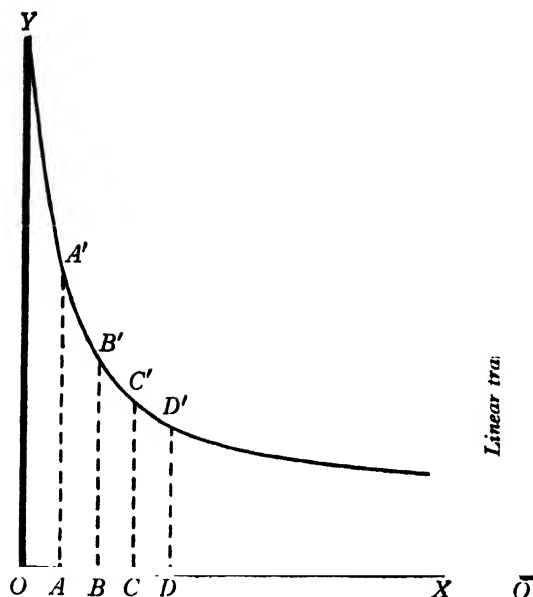


Figure 2A.

Linear exposure

Figure 2B.

§ 3. RESULTS

The negative film. Two films were used, the double-coated Ilford x-ray film and the Kodak Duplitized x-ray film, both without intensifying screens. These films are first soaked in water and then developed for $6\frac{1}{4}$ min. at 16°C . with good agitation in a tank of Agfa Rodinal of strength 1 in 20. The conditions are not critical, but an underdevelopment of 25 per cent results in a loss of the feebler intensities, while an overdevelopment of 25 per cent gives a dull background. The temperature of development may be varied provided that the duration is correspondingly adjusted; for instance at 18°C . the time is reduced to $4\frac{1}{4}$ min. No experiments were made at a temperature higher than 18°C . After being fixed in an acid bath the films are washed and are dried for 24 hr.

The positive film. For this the Kodak Commercial film or the Ilford Commercial orthochromatic film is satisfactory; the best results were obtained by a combination of the Ilford x-ray film as the negative with the Kodak Commercial film as the positive. It is for this combination that results are given. The film is developed for

5 min. at 17° C. in the following solution, which is one of the many Ilford developers:

Metol	2 g.
Sodium sulphite (crystals)	150 „
Hydroquinone	8 „
Sodium carbonate (crystals)	100 „
Potassium bromide	5 „
Distilled water, up to	1 l.

The components are to be dissolved in the order given.

It is necessary, before development, to saturate the emulsion with distilled water by soaking it for at least 2 min. After development the film is washed for about $\frac{1}{2}$ min., fixed, and after being washed, dried for 24 hr. The possibility of non-uniform development was found to be very greatly reduced by gentle brushing with a rubber strip moved uniformly over the emulsion every few seconds⁽⁴⁾. The conditions of development are not critical, and variations as for the negative film are allowable. A suitable printing exposure gives a minimum transparency of 0.01. The exposure tends to vary a little for different batches of film, and may do so by ± 20 per cent without causing serious error. The exposure used is equivalent to $2\frac{1}{2}$ sec. at 6 ft. from a small frosted 15-watt gas-filled lamp. If the Ilford film is used the exposure must be reduced to about one-half or one-third of this value.

The x-ray intensities on the negative, which gave curve α of figure 1A when printed on the positive film, give very nearly a straight line, figure 3; but if the printing exposure has been too short, this curve is convex on the upper side. To measure the actual ratio of intensities we use on the positive a uniform exploring beam of light large enough to cover the reflection, and place this beam first by the side of, and then over, the reflection. The difference in the light transmitted gives at once a measure of the x-ray intensity. If the reflection is so close to another that there is insufficient space to allow the exploring beam to be directed on to the background, the beam may be temporarily reduced in size and the observed background may be correspondingly increased; this is necessary because owing to scattering from unwanted sources, such as air, the background over the film is not constant. A test was made on an x-ray negative containing several reflections already measured on the mechanical integrator. A print of this film was made and the reflections were measured directly from the positive. The results are given in the table. The reflections at the end of the table are the weak reflections. For all such small exposures the characteristic of the negative film is linear and steep, and therefore, provided the background also is small, the reflections may be measured directly from the negative film; results obtained in this way are given in column 4. Measurements so made on the negative film are far more satisfactory than results evaluated by the mechanical integrator. In practice the best rapid method of measuring a group of intensities is to measure the weak reflections directly on the negative film and the remainder on the positive film, the same photometer serving for both sets of measurements. The correlating factor between them can be accurately found from a knowledge of (1) the slope of the characteristic, figure 1A,

of the negative film in the region of weak intensities, (2) the slope of the linear {transmission, exposure} graph, figure 3, of the positive film, and (3) the relative intensities of the exploring points used in the photometering of the negative and positive films. Full details are not given in this paper.

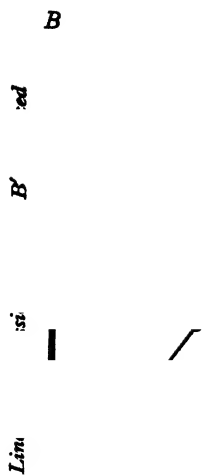
It will be noted that the differences between column 2 and column 3 of the table are considerably greater than the errors in a previous paper^(a), in which the ratio of the reflecting power of x-ray planes is given. This is because the intensities of these x-ray planes were each an average of a group of individual reflections, whereas in the present paper the individual measurements themselves are given.

Identification number of x-ray reflection	Integrated value by the mechanical integrator	Value by direct integration from positive film	Value by direct integration from negative film, valid only for weak reflections
1	6.5 ± 5 per cent	6.8	—
2	24.5 ± 4 "	24.9	—
3	13.7 ± 4 "	12.4	—
4	22.2 ± 7 "	23.2	—
5	37.6 ± 3 "	36.0	—
6	10.9 ± 9 "	10.4	—
7	7.6 ± 3 "	6.8	—
8	13.0 ± 5 "	12.2	—
9	22.4 ± 3 "	23.5	—
10	22.8 ± 3 "	21.8	—
11	53.7 ± 5 "	53.0	—
12	29.7 ± 3 "	30.5	—
13	6.2 ± 5 "	6.0	—
14	22.2 ± 5 "	26.0	—
15	27.7 ± 4 "	27.6	—
16	64.1 ± 5 "	63.5	—
17	55.1 ± 4 "	55.0	—
18	20.4 ± 4 "	20.0	—
19	1.8 ± 12 "	2.1	1.8
20	3.9 ± 12 "	3.4	3.9
21	3.4 ± 8 "	2.7	3.5
22	4.1 ± 8 "	3.9	4.2
23	4.3 ± 5 "	4.8	3.7
24	4.7 ± 5 "	3.7	4.2

§ 4. LIMITATIONS OF THE METHOD

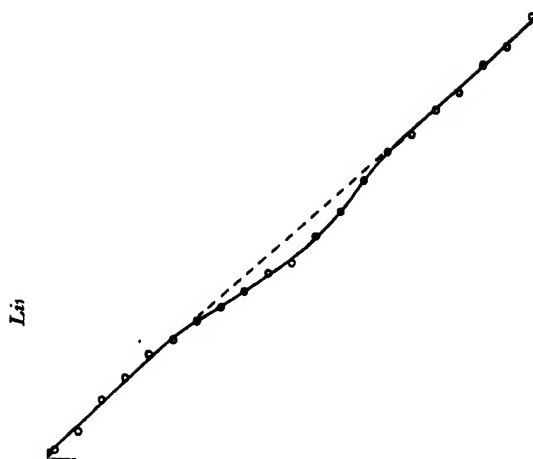
It is to be observed in figure 3 that a departure from linearity occurs in the region of greatest x-ray exposure, and this circumstance limits the range of measurable intensities. The restriction is not entirely new, because the flattening of the negative characteristic has, in the past, limited the range of accurately measurable intensities. The full range is usually covered by correlating a few photographs of differing exposures or by the artificial reduction of the stronger intensities by shutters incorporated in the x-ray camera^(s).

Fundamentally, a mechanical integrator affords the most accurate method of evaluating photographically recorded intensities, since it puts reliance on one film



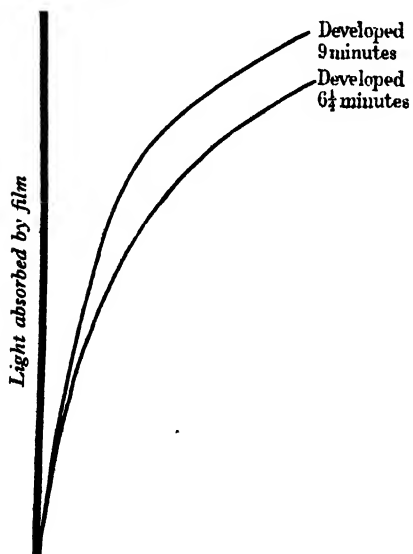
B' *X-ray exposure*

Figure 3. *B'* represents the light transmitted through positive at the foot of the (printed) wedge.



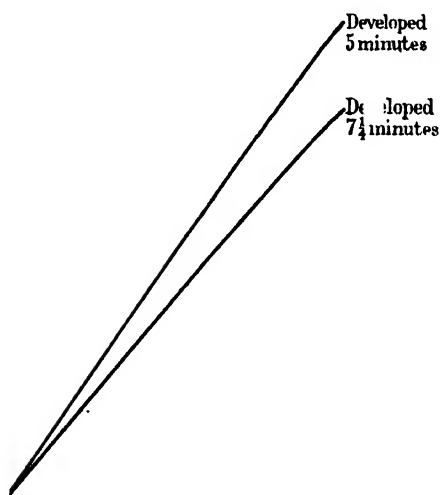
Printed X-ray exposure

Figure 4.



Linear X-ray exposure

Figure 5 A. Negative film.



Printed X-ray exposure

Figure 5 B. Positive film.

only, i.e. the negative. It must, however, be observed that full reliance is put on the master wedge which not infrequently is found to contain faults. Such faults are often not apparent until a positive print of the wedge is inspected; a distortion occurring in the resulting straight line is more easily observed than one occurring in the curved characteristic graph of the negative. An example of such an error shown by the positive is given in figure 4.

High precision in the measurement of individual x-ray reflections is seldom obtained and, although desirable, is in fact not absolutely necessary for all structure analysis work. Further, the infinite Fourier series itself requires some compromise between accuracy and convenience. There seems no doubt that in x-ray work integration by the positive film can serve a useful purpose by the rapidity of measurement and the simplicity of apparatus with which it is associated. The main disadvantage is that it involves the use of a second film with its attendant errors, one error being due to increase of development towards the edge of the film. This occurs also in the negative film and it is of interest to observe that in summation the two errors tend to mutual cancellation; overdevelopment of the negative increases the apparent x-ray intensities, figure 5A, and in the positive decreases them, figure 5B.

§ 5. ACKNOWLEDGEMENTS

In connexion with the latter part of this work the author is indebted to Dr J. Monteath Robertson, who had himself begun work on similar lines, for criticism and suggestions concerning the results, and for the loan of the x-ray negative containing the reflections given in table 1. The author also thanks Dr L. Lownds of Chelsea Polytechnic for his interest in the work, and Messrs Kodak, Ltd., for samples of film.

Note added in proof, 2 October 1938

Results for the Ilford Ilfex film also have been obtained. As a positive film the Kodak Commercial orthochromatic film was used and was treated in the same way as the Kodak Commercial film in this paper, except that the printed exposure was considerably reduced, being about 2 sec. at 7 ft. from a 5-watt frosted vacuum lamp, and giving a minimum transparency of about 0.04.

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A CONCAVE-GRATING VACUUM SPECTROGRAPH FOR WAVE-LENGTHS 15 TO 1000 Å.

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AND

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Read in title 14 October 1938

ABSTRACT. A vacuum spectrograph for work with soft x rays is described. It employs a 1-metre concave grating in the grazing-incidence position. The instrument is designed to permit the optical system to be adjusted before it is placed in the vacuum chamber, so that trial-and-error focusing may be minimized. It makes provision for varying the grazing angle without any necessity for readjustment. Tests of the instrument are described and discussed.

§ 1. INTRODUCTION

A CONCAVE grating in the grazing-incidence position was first used for the study of soft x rays by Osgood⁽¹⁾ and for the vacuum-spark spectra by Hoag⁽²⁾. Later some very fine spectrograms from the vacuum spark were obtained by Ericson and Edlén⁽³⁾ who used an instrument of Siegbahn's design, and more recently a number of publications⁽⁴⁾ have described vacuum spectrographs in which this arrangement has been devoted to one or other of these types of spectra. In the following paper we describe an apparatus of this kind which embodies some new features.

In designing the apparatus several requirements have been specially kept in mind. First, it was our object to build an instrument with good vacuum properties, and having as few welds and seals as possible. Secondly, it was desirable that gases from the spectrograph should not readily diffuse into the x-ray tube; this requires that the narrow slit of the optical system shall be the only opening for such diffusion. Thirdly, it was proposed to evolve an apparatus which would allow the adjustments of the optical system to be made in such a way as to minimize trial-and-error focusing. The apparatus was to cover the range 15 to 1000 Å. and to allow the use of different angles of incidence without readjustment. To permit of good grating reflection at the shortest wave-lengths, provision was required for a small minimum grazing angle, actually rather less than $2\frac{1}{2}^\circ$. The main purpose of the apparatus was the study of the soft x rays from solids. For this, high dispersion and resolution are of less importance than good intensity and ease of working. A short-focus instrument is therefore suitable, and the slits need not be inconveniently narrow. Finally, precautions were necessary to prevent the plates from being fogged by visible light entering the spectrograph through the slit.

§ 2. APPARATUS

The vacuum chamber. The vacuum chamber is a steel cylinder with a single longitudinal weld, and with wide flanges welded to the ends to receive end plates, which are of rolled brass. Each plate is ground to its flange, and in use the joint is made air-tight by the application of Apiezon sealing compound Q , which is smeared on externally. To facilitate the sealing process the plates are initially clipped tightly in position by the devices A_1 and A_2 , figures 1 and 3. The end plates have bevelled edges so as to receive the sealing compound readily. This method of sealing has been found both speedy and reliable, but experience has shown that more clearance between the outside edges of the end plates and the clips would be advantageous.

The slit-mounting. One of the end plates is pierced by a circular hole in which the slit-holder fits and in which it can rotate. The rotation is controlled by means of the screws S_1 , figure 4. The slit-blades are of stainless steel and are screwed to the holder, which is machined so that the blades lie in a plane approximately normal to the radiation. As the slit is only 1 cm. long and of the order of 0.01 mm. wide, there is little diffusion through it at low pressures. The flange on the slit-holder obviates any other leakage to the x-ray tube.

Optical bench. A machined brass bracket B , figures 1 and 4, is rigidly attached to the end plate which carries the slit. The runway carrying the grating carriage and camera is pivoted in this bracket at P , figure 3. It has on it a guide rail R , figures 3 and 4, machined to the radius of curvature of the Rowland circle. The grating carriage and camera are held closely in register with the rail by spring-loaded plungers. In making this register surface in the lathe, a false piece was fastened to the face plate on the opposite end of the diameter and turned with it to the correct diameter as measured by means of a gauge set to the measured radius of curvature of the grating. The camera and the bearing surface of the grating carriage are similarly turned to the required curvature.

Grating and grating-holder, figure 5. A Siegbahn glass grating having 576 lines per mm., rulings 1 cm. long, ruled portion extending over 2 cm., and radius of curvature 99.54 cm. is employed.* The movement of the grating backwards and forwards is achieved by means of the milled nut N , figure 4, acting against a spring pressing against a shoulder of the spindle Q . To avoid twist, the spindle is hexagonal in section. A ball joint J , figure 1, is provided to permit the rotation of the grating in its own plane and to allow it to be tilted backwards and forwards; the lever L , figures 1 and 4, imparts these motions. Finally, so that the grating may turn about a vertical axis, the whole system is mounted on a small table T , figure 4, which has a conical bearing. The axis of rotation passes vertically through the register surface and through the centre of the surface of the grating. A rotation should not, therefore, move the grating off its position over the Rowland circle rail. Adjustment of the tilt will, however, have a small effect on this position.

* In the usual mounting and with a grazing angle of 2.5° , this yields a dispersion of 2 Å. per mm. at 100 Å., and 2.7 Å. per mm. at 200 Å.

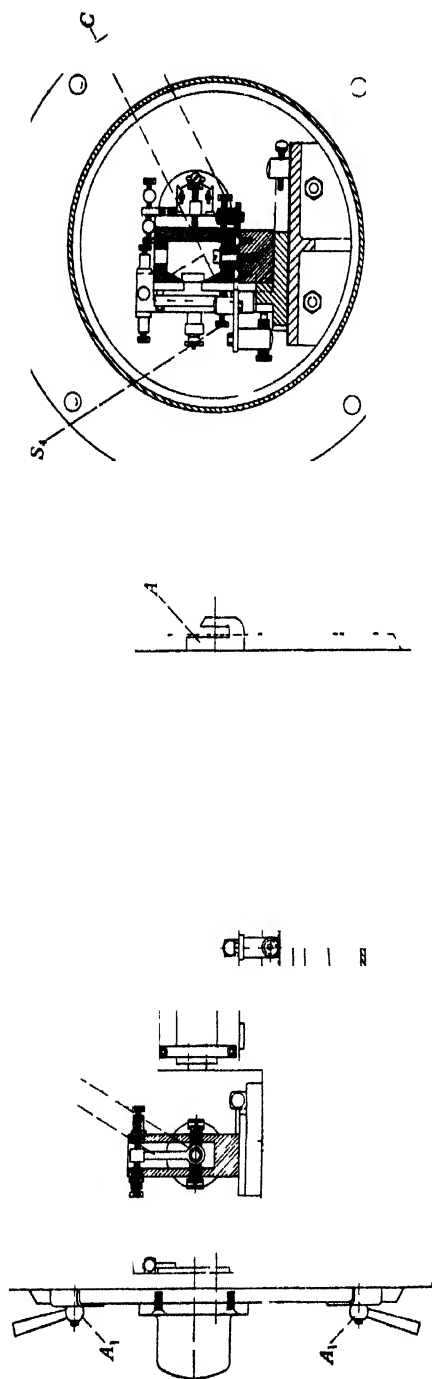


Figure 3.

2. S in d

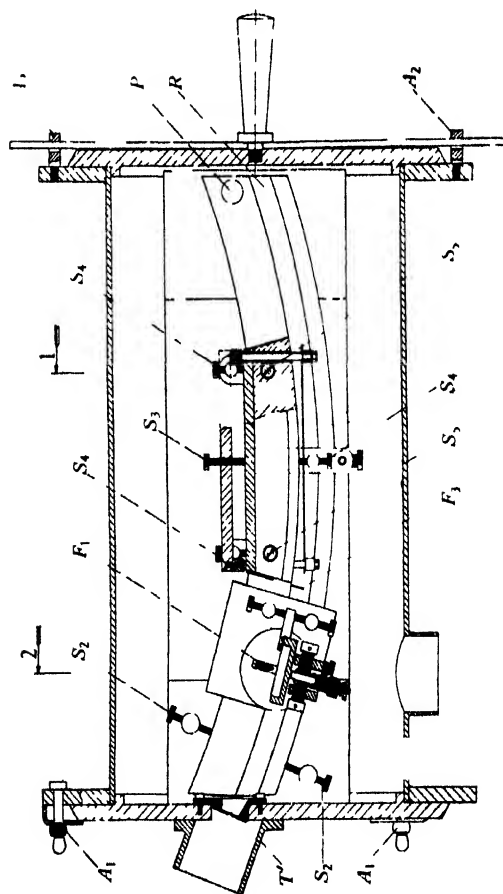


Figure 4. Section at 2, in direction of arrow.

A concave-grating vacuum spectrograph for wave-lengths 15 to 1000 Å. 929

The camera, figure 6. The camera is made in the form of a box open at the two ends—at one end to permit the entry of the radiation, at the other to let stray light pass out. After the box had been made, the side to receive the photographic plate was turned to the radius of the Rowland circle. The internal surfaces C, figure 2, are bevelled in order that no light reflected from them may strike the plate.

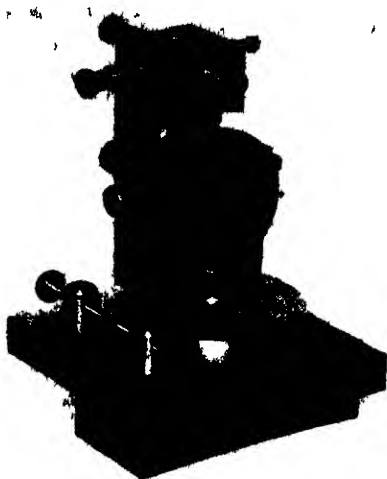


Figure 5

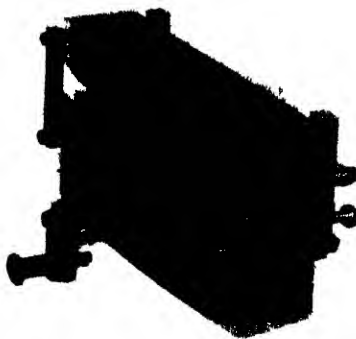


Figure 6.

To prevent the plate from being fogged from the back it is always mounted with a flexible sheet of brass behind it, and to minimize fogging due to scattering in the box the metal surfaces are coated with Aquadag.* The photographic plate is pressed to the curved surface of the camera by means of a clamp with a single central screw S_3 , figure 3, which actuates rods passing through the ends of the camera. The camera box is machined on its lower surface and can slide in a radial direction on the upper surface of its carriage. Trial-and-error focusing adjustments can therefore

* Kindly supplied by Messrs E. G. Acheson, Ltd.

be made by means of the screws S_4 , figures 2 and 3. The camera can be rigidly fixed to its carriage by the screws S_5 , figure 3. To permit these to be tightened, two holes are drilled in the top of the camera. The screen F_1 , figures 3 and 4, opposite the face of the grating, the sliding screens F_2 , figure 4, close to the slit, and F_3 , figure 3, at the entrance to the camera, are all designed to cut down the fogging of the plate.

Adjustment. The following adjustments are made before the apparatus is placed in the steel chamber.

(a) To locate the slit on the Rowland circle, the jig, figure 7, has been constructed. Its surfaces have been turned to the curvature of the Rowland circle. A slit-blade is removed and the jig is clamped to the rail with its point passing through the slit-aperture. The slit-holder is then rotated and the runway adjusted by screws S_2 , figure 3, until the surface of the jig makes contact with the slit-blade. The jig is then withdrawn and, with the aid of a microscope, the second blade is placed parallel to and at the required distance from the first.



Figure 7.

(b) To set the grating with its pole on the prescribed circle, an optical bench is placed immediately below the base bracket and so that the curved rail crosses it approximately at right angles. A pointer is mounted on a carriage on the bench. The jig is then placed on the circular track, and the pointer carriage is moved until the tip of the pointer touches the curved surface of the jig. The jig having been withdrawn, a microscope is mounted on a stand on the optical bench and slid along until it focuses on the end of the pointer. Finally, the grating carriage is placed on the track, moved until its centre is opposite the microscope, and then adjusted until the microscope focuses on the pole of the grating. Actually we focused on particles of dust on the surface.

(c) The next step is to make the grating, at its pole, tangential to the prescribed circle. First, the camera is adjusted so that its cylindrical surface is continuous with that of the camera carriage. This is done with the aid of a straight edge. Next, the camera is placed on the circular track at the end farthest from the slit. A fine hair is fixed vertically between the bevelled edges of the camera, and therefore on the circle, again at the end farthest from the slit. The grating and camera are now moved until slit and hair are equidistant from the pole of the grating. A distance piece is used for this adjustment. The grating is then rotated about a vertical axis until the image of the slit coincides with the hair. A microscope is employed to observe this coincidence.

(d) The grating must be tilted backwards or forwards until the image of the slit is as sharp as possible. This test is best made photographically.

(e) The final adjustment consists in the rotation of the grating in its own plane in order that the rulings may be made parallel to the slit. It is convenient to place a sodium lamp in front of the slit and to observe the *D* lines with an eyepiece. The grating is adjusted to make them as sharp as possible. This adjustment is not very critical.

In case the later settings may have affected them, the settings (b) and (c) should be checked and any necessary small readjustment should be made. The knife-edge screen F_1 , figures 3 and 4, is then placed in position. Care should be taken that this process shall not disturb the grating. The Rowland circle track is now placed in the vacuum chamber, the end plate, on which it is permanently mounted, being provided with two detachable handles to assist in this process. The metal tube T' ,

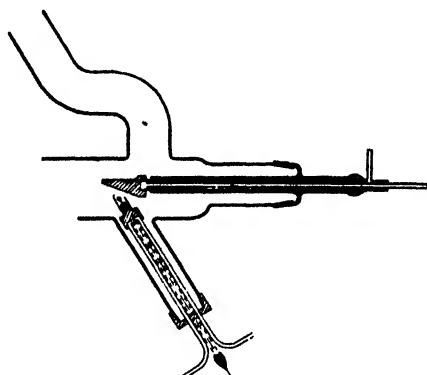


Figure 8.

figure 3, is next screwed into place in front of the slit, and the x-ray tube fitted over it. The joints are waxed. In the experiments carried out so far, a quartz x-ray tube has been employed, figure 8. The transparency of the quartz is convenient for setting the electrodes, but on the other hand a quartz tube is, of course, not so easily cooled as a metal one. The water cooling of the focusing cylinder around the filament was found to be necessary to check the deposition of carbon on the anticathode. For work with the vacuum spark, the anticathode and filament are replaced by conical water-cooled electrodes.

The x-ray tube and spectrograph are evacuated through independent wide tubes by a Metropolitan-Vickers oil diffusion outfit, the tubes uniting at the mouth of the pump. Large metal stopcocks are placed in each of the tubes so that the air can be let into the spectrograph at the end of an exposure without entering the pumps and oxidizing the hot oil. A connecting tube with stopcock allows the pressures in the spectrograph and x-ray tube to be equalized when air is being admitted to the spectrograph. Tombac bellows are included in the pumping lines to check vibration from the backing pump, and brackets are mounted on the spectrograph to prevent stresses on the x-ray tube when the bellows collapse. A

condensation trap is mounted in the x-ray tube line as a precaution. The bends in the x-ray tube outlet, figure 8, are to prevent electrons from reaching the seal of the pumping line.

§ 3. RESULTS

The vacuum properties of the spectrograph are very satisfactory. The breaking and making of the seal of the end plate for the purpose of loading the camera can be speedily carried out.

It was necessary to have photographic films or plates which could be bent to a radius of curvature of 50 cm. The thinnest glass plates that we could procure broke under such severe bending. Experience showed that films always buckled in the camera after the spectrograph had been pumped out. This, of course, rendered them useless for grazing-incidence work. Some mica sheets were then coated with emulsion for us by Messrs Ilford, Ltd.* The emulsion, however, tended to peel off under the vacuum conditions. Finally we succeeded in obtaining glass blanks of thickness 0.4 mm.,† and these, coated by Messrs Ilford, Ltd., have proved satisfactory.



Figure 9. Copper spark. Magnification 3.6.

For soft x-ray work in the region up to 100 Å., we had previously found Ilford Process plates very satisfactory. For vacuum-spark spectra we have employed Ilford Q 2 emulsion. This not only is satisfactory in the region above 100 Å., but also was found to be much more sensitive than the Process emulsion even for wavelengths as short as 14.5 Å. (nickel L_{α}). The plates are easy to handle and do not show chemical fog.

The precautions against optical fogging proved satisfactory. Of the screens F , that immediately at the end of the photographic plate proved essential. Without it, light entered the end of the glass plate, and, suffering multiple reflections, produced a periodic blackening along the emulsion. Reflection from the back of the grating was diminished by coating the latter with a mixture of lampblack and Canada balsam.

The apparatus was set up in the manner described above, and a number of exposures were taken with soft x rays down to 14.5 Å. and with the vacuum spark up to 800 Å. Adjustments (a), (b) and (c) were then remade and more exposures were made. In neither case was trial-and-error focusing employed. Figure 9 shows a copper vacuum-spark spectrogram taken with grazing angle $2\frac{1}{2}^{\circ}$ and slit-width 0.009 mm. The theoretical resolving power under these conditions is limited

* Through the courtesy of Dr O. Bloch.

† Procured from Messrs James Hetley and Co., 35 Soho Square, W. 1.

by the slit-width, and may be calculated from the formula

$$R = \frac{0.91 \rho \lambda m}{s \sigma},$$

given by Mack, Stehn and Edlén⁽⁵⁾, where ρ is the radius of curvature of the grating, s is the slit-width, σ the grating constant, and m the order. This yields the value 1160 at 200 Å. The observed value is not very different from this, and justifies our focusing system. For higher resolution the slit would need to be narrower, and then possibly some trial-and-error focusing might become necessary for the best results. On the other hand, in order to obtain good reflection for the shortest wave-lengths, we have used small grazing angles. With larger angles focusing errors would be considerably diminished. Again, we have here increased the risk of focusing error by employing a grating-width greater than the optimum.*

For soft x rays of the shortest wave-length, the diffracted beam makes a very small angle with the grating and with the photographic plate. Small errors in position of the surface of the plate consequently become of greater importance; it is therefore not surprising that the spectra are not consistently satisfactory below about 50 Å. However, with the grating which we employ, reasonably good intensity can be obtained in the fourth order, and we are able to examine the short-wave spectra without working in the more difficult portion of the Rowland circle. If the early orders of the short-wave spectra are to be examined, it would appear preferable to employ the Söderman method⁽⁴⁾, in which the plate is mounted perpendicular to the radiation.

§ 4. ACKNOWLEDGEMENTS

The spectrograph was built by Mr T. Gurman in the workshops of the Mechanical Engineering Department of this College. The apparatus has been erected and tested in the Physics Department. We have pleasure in expressing our gratitude to the respective heads of these Departments, Prof. G. T. R. Hill and Prof. E. N. da C. Andrade. In addition, we are indebted to various members of the Engineering Faculty for valuable discussions.

Finally we are indebted to the Dixon Fund of the University of London for a grant to one of us (F. C. C.) which made the construction of the apparatus possible.

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* The restricted size of the spark gap, however, probably diminished the effective size of the grating slightly. The width for maximum resolving power has been calculated by Mack, Stehn and Edlén⁽⁵⁾.

THE ACCURACY OF RECTIFIER-PHOTOELECTRIC CELLS

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ABSTRACT. The effect of a resistance R in series with a rectifier-photoelectric cell on (a) the linearity of the response and (b) the temperature coefficient of the sensitivity has been investigated. In order that no restriction should be imposed on R by the effective sensitivity, the photoelectric current was measured by compensation. The light sources used in these experiments were tungsten filament vacuum lamps operating at a colour temperature of approximately 2400°K . The temperature coefficient of the cell is always least when $R=0$, but is not then generally zero. The approach to linearity is generally closest for a finite value of R which is usually between 100 and 1000 Ω . But no value of R will avoid errors of 1 per cent if linearity is assumed over a range of 0 to 240 lux. The observations can be explained qualitatively, but not completely, by assuming the presence of a series resistance inside the cell in addition to the shunt resistance. These two resistances do not vary in the same manner with temperature or with illumination. Some practical conclusions are given in the final paragraph.

§ 1. THE PROBLEM

THE output of a rectifier cell is usually measured by connecting it in series with a resistor of resistance R , as shown in figure 1 but without the dotted element, and measuring the current I through the resistor. The resistor may be a galvanometer or microammeter; but if high accuracy is required, it will generally be a standard resistor and the voltage V across it will be measured with a potentiometer. The relation between I and L , the luminous flux incident on the cell, can then be represented by

$$I = \alpha L \{1 - f(L, R)\} \quad \dots\dots(1),$$

where $f=0$ when $L=0$.

The earlier investigators, aiming at an accuracy not greater than 1 per cent, concluded that f was always positive and increased both with L and R . This conclusion was explained by taking into account the shunt resistance r of the cell, which is known to decrease as L increases; the circuit should include the dotted element, the cell C being regarded as a resistanceless source of current I_0 , proportional to L . Then

$$f(L, R) = R/(R+r) \quad \dots\dots(2).$$

It followed that, if R could be made zero, f would always be zero and the cell would be truly linear.

More recent experiments aiming at a higher accuracy, and in particular the very careful work of Buchmüller and König⁽¹⁾, throw doubt on this conclusion. They seem to show that f may sometimes be negative and that, even if it is positive, it does not necessarily tend to zero with R . It may be said at once that this is the result to which our experiments lead. But previous work has been hampered by the impossibility of reducing R without limit while retaining adequate sensitivity in the measurement of the current; for, whatever is the nature of R in figure 1, the sensitivity inevitably decreases with R .

Restrictions on the value of R can be removed by using the compensation method of measuring I , proposed by Campbell and Freeth⁽²⁾. Their circuit is shown in figure 2, but the resistance R was not mentioned originally. The rheostat Q is varied until the galvanometer G is undeflected, showing that there is no potential

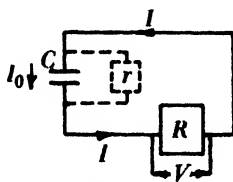


Figure 1.

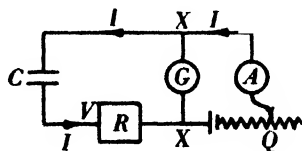


Figure 2.

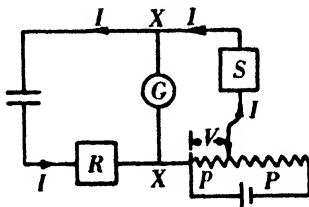


Figure 3.

difference between the points X, X ; then the current flowing through the direct-reading instrument A must be the same as that flowing through R . The sensitivity is determined wholly by that of A , which may have any resistance; R does not affect the current sensitivity and may be zero. A simple modification of figure 2, more convenient in practice, is shown in figure 3. Here P is an accurate potentiometer, such as might be used for measuring V in figure 1 but with a higher range. If V is read on the potentiometer in the ordinary way, i.e. as proportional to p/P , where P is the total resistance of the potentiometer, the maximum relative error involved in taking I to be proportional to V is $P/4S$, where S is the resistance through which the compensating current passes. If, for example, $S=30,000 \Omega$, $P=30 \Omega$, the maximum error is 1 part in 4000. It is to be observed that the sensitivity, taken as the value of V corresponding to a given I , is increased in the ratio of S to R as compared with that pertaining to figure 1. In practice this means that, while V is in millivolts in figure 1, it is in volts in figure 3.

This method has been used to determine the departure from linearity, in dependence on the value of R , of several rectifier cells of different types; that is to

say, the quantity $f(L, R)$ has been determined; the dependence on R of the temperature coefficient of I has been observed also. L was varied, as it must be in any experiments aiming at accuracy, by addition. The principle is well known. The cell is arranged so that it can be exposed to any combination of N independent sources of light. The sources are adjusted so that each of them, acting apart from the others, produces the same current in the cell; each source then throws the same amount of light L_m on the cell. The light received by the cell when n sources act together is nL_m .

However, as many workers have found, it is not easy to apply the principle exactly. It is necessary to ensure that the exposure of the cell to light from one source shall not change the light received from another; it is necessary also to keep the temperature of the cells constant. Accordingly we give details of our apparatus and of the conduct of the observations.

§ 2. APPARATUS

The apparatus is shown diagrammatically in figures 4 and 5. It was constructed in 1933,* and was originally used for investigations into the linearity of response of emission-type vacuum photocells. In the work on these cells the stability of the apparatus had been shown to be very high, and repetition accuracies of the order

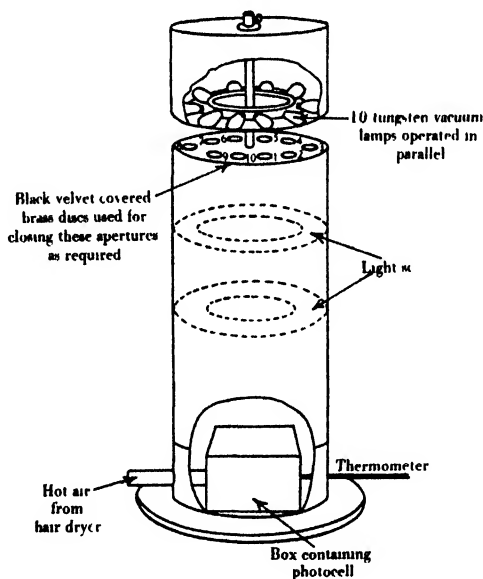


Figure 4. General arrangement of apparatus.

of a few parts in ten thousand had been recorded; vacuum cells had been proved linear to one part in a thousand; the suitability of the apparatus for the purpose in view had therefore been already established.

* It was demonstrated at the Physical Society's Exhibition in January, 1934.

Ten straight-wire cage-filament tungsten vacuum lamps, mounted axially and rigidly clamped, form the light sources. These are connected in parallel by leads soldered to the lamp terminals, in order to avoid the possibility of instability due to poor contacts. The lamps are operated from a battery and kept at a constant voltage throughout the tests by means of a potentiometer. In the present investigation, the operating temperature of the filaments was approximately 2400°K . Below each lamp is an aperture which can be closed, as required, by means of a brass disc covered with black velvet. The location of the apertures, lamps and photometric screens is such that the casings of the lamps and of the photocells can be kept in a fixed position, and yet there is sufficient room to enable the discs for covering the holes to be manipulated without any risk of stray light reaching the photocell.

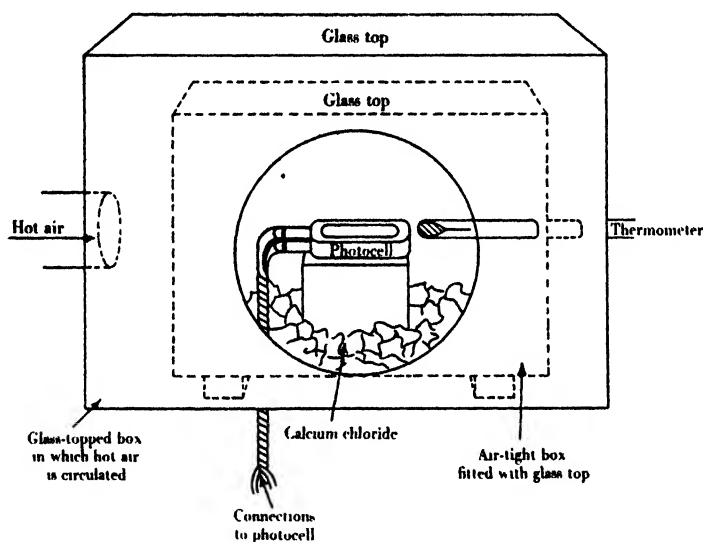


Figure 5. Sketch showing details of double box containing photocell.

The photocell under test is housed in a small box with a glass top, as shown diagrammatically in figure 5. A small quantity of calcium chloride is put in the bottom of the box in order to prevent condensation on the glass window, and a thermometer is arranged with its bulb adjacent to the photocell. This is enclosed in an outer container, and air is circulated between the walls of the two boxes by means of an electric hair-dryer, the temperature of the air being controlled by regulating the current through the heater coils of the dryer.

Precision potentiometers were used for measuring the potential drops in the photocell circuits.

§ 3. TESTS ON APPARATUS

Before the investigations were begun tests were again made to determine the reliability of the photometric arrangement. It was found that the error introduced by light reflected from the underside of the velvet-covered discs could not be

detected, and was therefore negligible. Tests on the photometric screening also showed that no measurable error could arise from this cause.

When measurements of the resistance of the photocells were being made for this investigation, reversal measurements indicated that the cells did not rectify appreciably under these conditions. With the various circuits used, no contact e.m.f. could be detected which would affect the validity of the measurements.

The double container for the photocell under test was very satisfactory from the point of view of thermal stability, and no difficulty was experienced in maintaining constant air temperatures in the inner container to within $\pm 0.5^\circ \text{C.}$, throughout any one series of measurements.

§ 4. METHOD

Table 1 shows a typical series of observations.

Table 1. Cell No. 8; $R=0$

n	I_n ($\mu\text{a.}$)	J_{10} ($\mu\text{a.}$)	a_n	A_n	J_n ($\mu\text{a.}$)	J_{10} ($\mu\text{a.}$)	B_n	$\frac{A_n - B_n}{A_n}$ (per cent)	$\frac{\sum \delta_n L}{n L_m}$ (per cent)
1	1.388	13.950	0.0994	0.0994	—	—	0.0994	0	+4.4
2	1.318	13.948	0.0945	0.1939	2.710	13.807	0.1963	-1.24	+1.8
3	1.348	13.938	0.0967	0.2906	4.120	13.800	0.2987	-2.79	+1.8
4	1.233	13.900	0.0913	0.3819	5.440	13.793	0.3944	-3.28	+0.3
5	1.443	13.883	0.1040	0.4859	6.943	13.783	0.5048	-3.90	+2.1
6	1.213	13.868	0.0875	0.5734	8.213	13.738	0.5982	-4.39	+0.4
7	1.448	13.850	0.1046	0.6780	9.713	13.728	0.7083	-4.43	+1.3
8	1.388	13.833	0.1002	0.7782	11.117	13.708	0.8120	-4.35	+2.2
9	1.093	13.820	0.0792	0.8574	12.268	13.680	0.8976	-4.69	+0.1
10	1.303	13.807	0.0945	0.9519	—	13.660	1.0000	-5.06	0

Mean 0.09519

$$\sum_1^n A_n = 5.2906; \quad \sum_1^n B_n = 5.5097; \quad 1 - k = \frac{\sum B_n}{\sum A_n} = 1.0415.$$

Here I_n is the current with the n th aperture alone open, J_n is the current with all the apertures 1 to n open, $a_n = I_n/J_{10}$, $A_n = \sum_1^n a_n$ and $B_n = J_n/J_{10}$.

I_n is measured first in the order 1 to n , each measurement being taken between a pair of measurements of J_{10} ; J_n is then measured similarly. The whole series of measurements takes about 15 min. Of course $B_1 \equiv A_1$ and $B_{10} \equiv 1$. The differences in J_{10} indicate the repetition accuracy of a single absolute measurement. It may be questioned whether relative accuracy, which alone matters, is increased by taking a_n or B_n instead of I_n or J_n . The answer is that a review of the whole series of measurements shows that regularity and consistency are thereby increased, but it is impossible to say what residual inaccuracy due to the variations of J_{10} remains. The variations are probably due partly to variations in temperature of the cell, independent of the incident light; the effect of this part must be eliminated almost

completely. But they are probably partly due to the effect of light on the cell in changing its temperature or causing fatigue. The effect of this part will not be completely eliminated; for the light incident when I_n or J_n is measured is always less than when J_{10} is measured. It is thought, however, that no a_n or B_n is in error by more than 2 parts in 1000, and that the average error does not exceed 1 part in 1000.

Some of the measurements were repeated by the method of figure 1, with the same value of R . The values of A_n and B_n should be precisely the same, whichever method is used; for I should be the same whether the p.d. across XX is made zero by connecting these points by a conductor of zero resistance, figure 1, or by introducing a compensating current so as to make the deflection of G zero, figure 3. Some puzzling discrepancies were found; but they could not be repeated, and it was concluded that they arose wholly from the greater experimental error of figure 1, which was due to the much lower sensitivity. No consistent difference could be found between the mean sensitivity of the cell in amp./lumen and its variation with temperature as measured by one method and the same quantity as measured by the other.

We have now to ask what information is given by these measurements. Let L_n be the illumination on the cell through the n th aperture. All the L_n 's are not exactly equal; let L_m be the mean of the L_n 's, so that

$$L_n = L_m + \delta_n L.$$

Let $L_n' = \sum_1^n L_n$ be the illumination through all the apertures 1 to n . Since R is constant through a series, we can write $f(L)$ for $f(L, R)$. Then we have, omitting terms in powers of f higher than the first,

$$I_n = \alpha L_n [1 - f(L_n)] \quad \dots\dots(3),$$

$$J_n = \alpha L_n' [1 - f(L_n')] \quad \dots\dots(4),$$

$$a_n = (L_n/L_{10}') [1 - f(L_n) + f(L_{10}')] \quad \dots\dots(5),$$

$$A_n = (1/L_{10}') [L_n' \{1 + f(L_{10}')\} - \sum L_n f(L_n)] \quad \dots\dots(6),$$

$$B_n = (1/L_{10}') L_n' \{1 - f(L_n') + f(L_{10}')\} \quad \dots\dots(7),$$

$$\frac{A_n - B_n}{A_n} = \frac{L_n' f(L_n') - \sum L_n f(L_n)}{L_n' \{1 + f(L_{10}')\} - \sum L_n f(L_n)} \quad \dots\dots(8),$$

$$= f(L_n') - \frac{\sum L_n f(L_n)}{L_n'} \quad \dots\dots(9).$$

If all the $\delta_n L$'s were zero, we could write in place of equation (9)

$$\frac{A_n - B_n}{A_n} = f(nL_m) - f(L_m) \quad \dots\dots(9').$$

The ratio of the right-hand side of equation (9) to that of equation (9') differs from 1 by less than $\sum \delta_n L/nL_m$. The values of this quantity, derived from A_n on the assumption of linearity over the small range $\delta_n L$, is given in the last column of

table 1. They are thus percentage corrections to be applied to the preceding column. It will be seen that the difference between equation (9) and equation (9') can never lead to an absolute correction amounting to 0.1 in the tabulated value of $(A_n - B_n)/A_n$. Since the tabulated values are subject to an experimental error of this order, we may take them as giving $f(nL_m) - f(L_m)$.

These values may now be plotted against n or $L = nL_m$; see curve 8 of figure 6. The resulting curve defines a function $F(L)$ which has this significance, to our order of approximation. If we calibrate the cell by observing the current I_c due

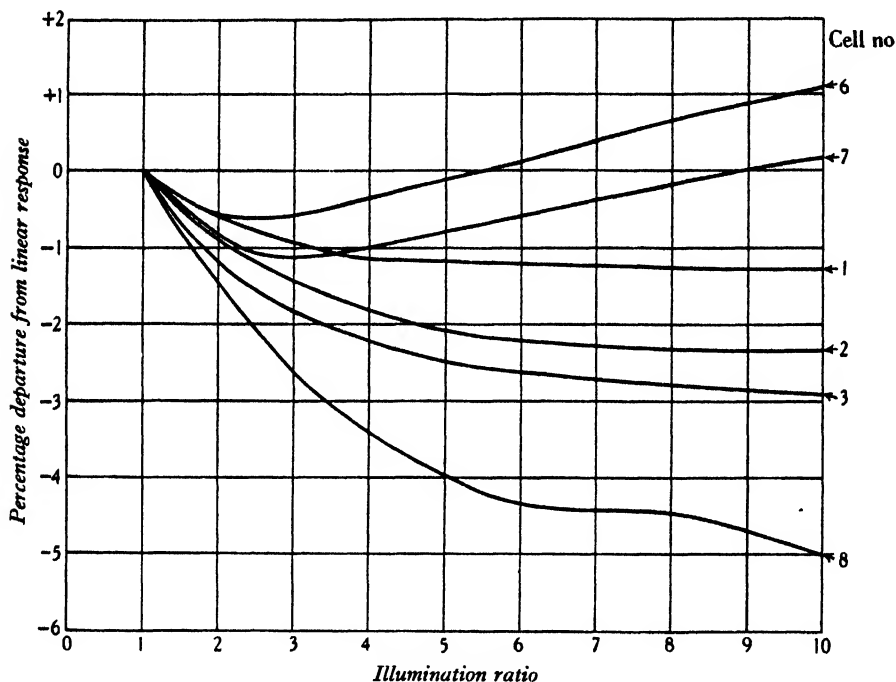


Figure 6. $F(I, \circ)$.

to the known illumination L_c and find L_c , equal to βI_c , then the relation between any known illumination L and the current produced by it is

$$L = \beta I \{1 - F(\beta I) + F(\beta I_c)\} \quad \dots\dots(10).$$

In other words $F(\beta I) - F(\beta I_c)$ is the relative error involved in assuming linearity based on the single calibration. It is to be observed that, though $F(L)$ has been deduced on the assumption that the calibration is made with the illumination L_m , equation (10) is true to our order of approximation whatever the illumination used in calibration, so long as it is such that $f(L)$ is always small. Accordingly, $F(L)$ gives all the information required for the practical purpose of estimating or correcting errors arising from the assumption of linearity.

Strictly $F(L)$ is given only for values of L equal to nL_m , where n is an integer from 1 to 10. To obtain $F(L)$ for other values between 0 and nL_m we should have

to interpolate, and to extrapolate to zero. The curves are sometimes so irregular that this process, and especially the extrapolation, would be precarious; accordingly, it has not been effected. Of course, the only way to remove this uncertainty is to repeat the observations with a smaller value of L_m .

For a general survey of the results obtained with different cells, another procedure is desirable. If we knew the curve relating I and L and intended to assume linearity in our measurements, we should fit to the curve the best straight line, and assume the relation given by this line. The cell would be more linear, the less the average departure of the curve from the straight line. The procedure is not perfectly determinate, because the expression "best straight line" is ambiguous; and it is not worth while to discuss in detail how the procedure might be carried out on the basis of our observations. But consideration will show that an indication of the average departure is given by the quantity R , equal to $1 - (\Sigma B_n)/(\Sigma A_n)$, where ΣB_n and ΣA_n are respectively the sums of columns 8 and 5 in table 1. $(1 - k)$ is roughly the ratio of the slope of the line through the origin and the point (I_m, L_m) , which approximates to the tangent to the curve at the origin, to the slope of the best straight line. k is zero if the curve is linear, or if there is no general tendency of I/L to increase or decrease with L ; it is positive (or negative) if I/L generally decreases (or increases) with L , so that $F(L)$ is predominantly positive (or negative). Accordingly, we may say roughly that the curve is the more linear the less the value of $|k|$. It is to be observed that a positive k implies a normal departure from linearity, such as is known to be due to a large value of R ; a negative k implies an opposite departure such as has hitherto been regarded as abnormal.

§ 5. RESULTS

The results of our observations can now be summarized in table 2 and figures 6, 7, 8.

In table 2, column 1 gives the numeral assigned to the cell. All the cells were of the selenium, not the cuprous-oxide, type, and all were commercial products; but since we do not know whether their makers would regard them as typical of their manufacture, it would not be proper to give the makers' names. Cell no. 8 was covered with a filter designed to make its sensitivity agree with the luminosity curve; this is why its sensitivity is relatively low. The other cells were bare. Column 2 gives the area of the cell. Column 3 gives the resistance R_c of the cell, measured in the dark with a small current at 30°C .; column 4 gives the temperature coefficient γ of the resistance, equal to $1/R_c \cdot dR_c/dT$ and measured over the range 20° to 40°C . γ is not always strictly constant over this range, but a mean value, sufficient for our purpose, is assigned. Column 5 gives R in figure 3. Column 6 gives σ , the sensitivity, measured in microamperes for an illumination of 240 lux (L_{10}') at 30°C . Column 7 is the temperature coefficient θ of the sensitivity, equal to $1/\sigma \cdot d\sigma/dT$ between 20° and 40°C .; it again is a mean value. Column 8 gives k . In figures 6, 7, 8 some of the $F(L)$ curves are plotted as described. Figure 6 collects those for which $R=0$; figure 7 shows how $F(L)$ varies with R in cell no. 8;

figure 8 shows $F(L)$ for that value of R which gives minimum $|k|$ in each cell. It is not shown for cell 6, for which $|k|$ is least when $R=0$.

The measurements on cells 4, 5 are much less satisfactory than the others, for these cells show marked fatigue. It is not easy to obtain measurements to 1 part in 1000 and, if a measurement is obtained, its interpretation is doubtful. The cells are included in order to show the faults of really bad cells. In these cells $F(L)$ is so large when $R=0$ that it cannot be plotted on the scale of figure 6.

Table 2

Cell no.	Area (cm ²)	R_c at 30° C. (Ω.)	γ (per cent per °C.) 20° to 40°	R (Ω.)	σ at 30° C.	θ (per cent per °C.) 20° to 40°	k
1	5.4	540	-3.5	0	42.9	-0.20	-0.010
				200	—	—	-0.005
				250	26.4	-1.44	+0.0048
2	5.4	1105	-3.7	0	32.6	-0.62	-0.022
				100	—	—	-0.0108
				200	24.8	-1.84	+0.010
3	5.4	2560	-2.3	0	42.6	-0.08	-0.025
				200	35.8	-0.58	+0.0038
4	5.28	9410	-2.3	0	45.1	+0.14	-0.119
				250	—	—	-0.073
				500	—	—	-0.045
				750	—	—	-0.050
				1000	32.9	-0.78	+0.0098
5	5.28	3570	-2.3	0	37.9	+0.51	-0.280
				1000	—	—	-0.092
				2000	17.1	-0.77	+0.028
6	5.4	4710	-4.8	0	63.5	-0.28	+0.0048
				100	58.5	-0.38	+0.0128
7	5.4	2170	-4.8	0	62.0	-0.51	-0.0038
				100	53.8	-0.6	+0.002
				500	—	—	+0.065
8	12.6	3530	-3.0	0	13.8	-0.07	-0.042
				250	—	—	-0.050
				500	—	—	-0.044
				1000	—	—	-0.021
				1250	—	—	-0.0098
				1350	9.02	-0.88	+0.0008
				1500	—	—	+0.0098

The following features of table 2 should be observed: (1) k is usually negative when $R=0$; the departure from linearity is abnormal. As is to be expected, k is always positive for sufficiently large values of R . Accordingly there is usually a value of R other than zero at which k is most nearly zero and the cell most nearly linear, according to our criterion. (2) Even when k is most nearly zero, the maximum value of $F(L)$ is always greater than 1 per cent. (3) The value of R which makes $|k|$ least tends to increase with R_c ; but there is no simple relation between this value and R_c which would enable the value to be found without calibration. (4) θ , the rate of variation of sensitivity with temperature, is always least when $R=0$; as is to be expected, the sensitivity is always greatest when $R=0$.

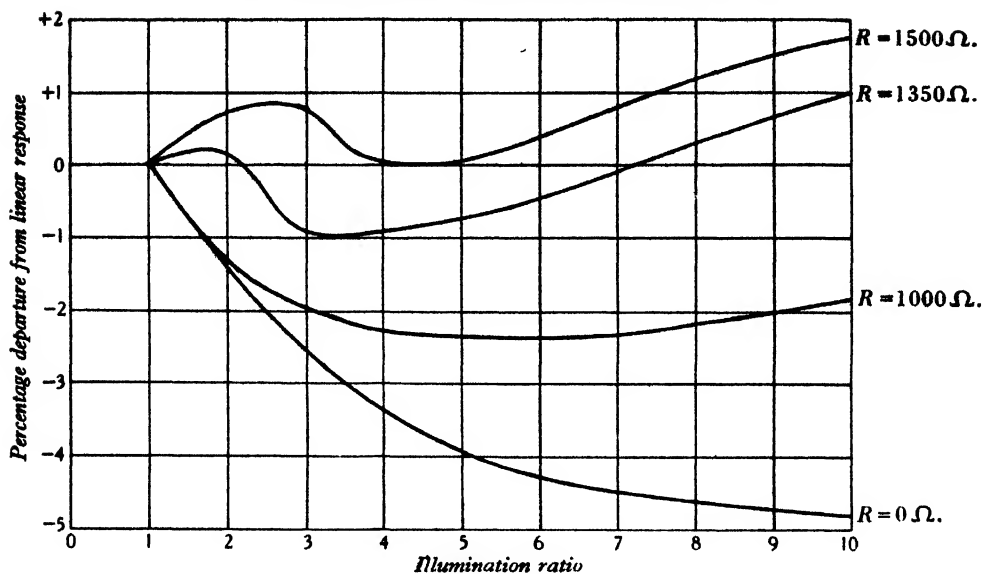


Figure 7. $F(L, R)$ for cell no. 8.

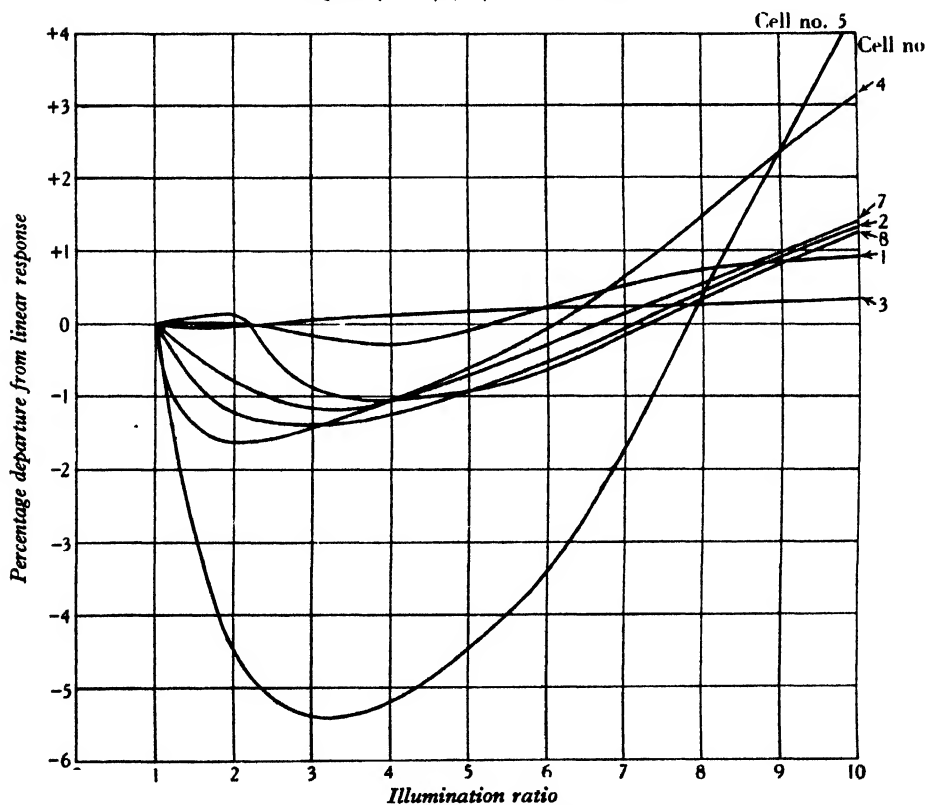


Figure 8. Best $F(L, R)$.

§ 6. THEORY

The simplest way of explaining qualitatively the negative values of k and of $F(L)$ when $R=0$ is to modify figure 1 by the introduction of a series resistance S , inseparable from the cell, as shown in figure 9. S , like r , decreases as L increases, as will be indicated by the suffix L . Then we have

$$I = I_0 \frac{r_L}{R + r_L + S_L} \quad \dots\dots(11).$$

$$\text{When } R=0, \quad \frac{I_0}{I} = \left(1 + \frac{S_L}{r_L}\right) \quad \dots\dots(12),$$

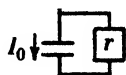


Figure 9.

the sign of $d(I_0/I)/dL$, which is the sign of k and of $F(L)$, will be the sign of

$$\left(\frac{1}{S_L} \frac{dS_L}{dL} - \frac{1}{r_L} \frac{dr_L}{dL}\right)$$

Hence we can explain a negative value of k at $R=0$ by supposing that the relative decrease of S_L with increase of light is more rapid than that of r_L . On the other hand, if R is sufficiently large compared with $(r_L + S_L)$, the sign of k will always be that of $-dr_L/dL$, that is to say positive.

If, as perhaps we should expect, differences in the relative variation with light were always associated with differences of the same sign in the relative variation with temperature, it would follow that, when $R=0$, negative k is always associated with positive θ . Table 2 shows that this is not the case, but there is a tendency for more positive or less negative θ to be associated with more negative k .

Of course it is not to be expected that the theory should be quantitatively accurate, for it cannot be really true that the cell can be analysed into three entirely separate elements, a current generator, a shunt and a series resistor. Accordingly, it has not been thought necessary to make all the measurements required for a complete quantitative test. But it may be worth while to indicate how a test might be made.

Equation (11) can be written

$$R = -(r_L + S_L) + r_L I_0 \frac{1}{I} \quad \dots\dots(13).$$

Hence, by measuring I for the same illumination (and therefore the same I_0 , r_L , S_L) but different R 's, and plotting R against $1/I$, we should obtain a straight line whose

intercept gives us $(r_L + S_L)$. We know $(r_0 + S_0)$, the resistance of the cell in the dark, when $I_0 = 0$, and its relative temperature coefficient γ . If we write δ for the relative temperature coefficient of r_L , i.e. $1/r_L \cdot dr_L/dT$, we have

$$\theta = \delta - \frac{r_L + S_L}{R + r_L + S_L} \gamma_L \quad \dots\dots(14).$$

We may probably take r_L , the temperature coefficient of $(r_L + S_L)$, to be independent of L , and therefore may identify γ_L with γ in table 2. If then θ_0 is the value of θ when $R = 0$, we have

$$\delta = \theta_0 + \gamma \quad \dots\dots(15),$$

and δ can be calculated from table 2. Since we know $(r_L + S_L)$, we can then calculate θ for other values of R and compare them with the observed values.

It should be observed that we cannot estimate r_L from the slope $r_L I_0$ of the line (13), for we cannot know I_0 . According to equation (11) I_0 is not equal to I for any value of R at any illumination.

Equation (13) is very well fulfilled for cell no. 8 and somewhat less well for cell no. 4. For the other cells the data are insufficient to test the relation. But by calculation, $(r_L + S_L)$ being estimated in all cases from the value for $R = 0$ and the other value at which the temperature coefficient of the sensitivity was measured, we arrive at the result shown in table 3, in which the observed and calculated values of θ are compared. The error in $(r_L + S_L)$ is often very large, but then the effect of an error is correspondingly small. The agreement is by no means perfect, but it is perhaps sufficient to indicate that the theory has some foundation and that there is something of the nature of a series resistance whose variation with temperature and illumination is not the same as that of the shunt resistance.

Table 3

Cell no.	$(r_L + S_L)$	θ_0	γ	δ	R	$\frac{r_L + S_L}{R + r_L + S_L} \gamma$	θ calculated	θ observed
1	397	-0.20	-3.5	-3.7	250	-2.15	-1.55	-1.45
2	639	-0.68	-3.7	-4.3	200	-2.8	-1.5	-1.8
3	1070	-0.08	-2.3	-2.38	200	-1.94	-0.48	-0.6
4	2680	+0.14	-2.3	-2.18	1000	-1.68	-0.5	-0.8
5	1640	+0.51	-2.3	-1.8	2000	-1.04	-0.8	-0.8
6	1180	-0.28	-4.8	-5.0	100	-4.4	-0.6	-0.35
7	657	-0.51	-4.8	-5.3	100	-4.2	-1.1	-0.6
8	2540	-0.1	-3.0	-3.1	1350	-1.98	-1.1	-0.9

§ 7. PRACTICAL CONCLUSIONS

If measurements cover the whole range from 0 to 240 lux, and if it is assumed that the cell is linear, then errors of at least 1 per cent will be made, whatever the illumination at which the cell has been calibrated and whatever the value of the external resistance R . In a bad cell the errors may amount to 5 per cent, even with the best value of R . Cells with high internal resistance are not in general better

in respect of linearity than cells with low internal resistance. The experiments are not sufficient to determine what errors are introduced by assuming linearity over some lower range of illumination, say 0 to 20 lux. But they do not suggest that, even over that range, the errors will be less than several parts in 1000.

If an accuracy better than 1 per cent from 0 to 240 lux is required, the cell must be calibrated by addition, as described above, over the whole range. The calibration must be repeated at least once a day. It is then best to make R equal to 0 and to use the compensation circuit of figure 3, for the effect of temperature variations is then least. If linearity is to be assumed, then the errors arising from that assumption will generally be least when R has some value between 100 and 1500 Ω ., which can only be determined by a full calibration. But the value is substantially constant for a given cell over considerable periods of time. However, use of this value of R will increase the temperature variations materially.

For a given value of R there is no difference between the behaviour of the circuits of figure 1 and figure 3 except in respect of sensitivity. The circuit of figure 3 is always the more sensitive, and permits the use of a resistance R smaller than is practicable with the circuit of figure 1. If a null method of measuring the current is to be used in any case, the circuit of figure 3 has no compensating disadvantage, but that of figure 1 has the advantage that it can be made direct-reading. If linearity is to be assumed, the superior accuracy of null methods is illusory; the ordinary direct-reading circuit shown in figure 1 is then as good as any other, unless temperature variations are likely to be so serious that it becomes important to make R equal to 0.

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A PROBLEM IN COIN-TOSSES

By S. R. SAVUR

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ABSTRACT. The paper discusses data given by Norman Campbell, on the tossing of a coin, and questions his conclusion that the particular series quoted does not define a chance. A theoretical investigation is made of the limits within which the heads-to-tails ratio obtained by tossing a coin a given number of times may be expected to diverge from unity, and a practical study of the drawing of coloured balls from a container is described. The conclusion reached is that the ratio obtained in practice converges towards the ratio to be expected on theoretical grounds provided that the number of trials is very great indeed.

IN his paper "The statistical theory of errors"⁽¹⁾ Norman Campbell has tried to show that statistical methods are irrelevant to "problems that arise in drawing conclusions from observations". It is not the purpose of this short note to discuss how far Campbell has succeeded in proving his point, but rather to consider a conclusion drawn by him, namely, that the application of statistical methods to the experimental results obtained even in a problem "to which every one admits statistics to be relevant" does not give definite results.

The problem considered by Campbell is the tossing of a coin. His comments, pp. 802-3, on the results of the experiments are: "It is unusual to have as many as 20 measurements made in conditions so similar that, on any reasonable theory of error, they can be regarded as a sample drawn from a single collection. How inadequate such a sample is to prove the existence of a chance is illustrated by figures 1 and 2. These show the results of 500 tosses of a coin recorded for this occasion. . . . The first 20 tosses suggest no characteristic chance; the first 90 suggest one definitely greater than 0.5; the first 500 leave the whole matter doubtful. Many more tosses would be required to convince anyone that the chance really exists."

The impression one gets from these remarks is that although 20 experiments are usually believed to be sufficient by statisticians, yet even a number of experiments (or tosses) as high as 500 in the case of a coin, to which statistical methods are undoubtedly applicable, has been found insufficient for the purpose, and that hence there must be something wrong in statistical methods as advocated at present.

This view is not correct because it depends upon the assumption that about the same number of experiments will be required in all cases, an assumption that does not appear to be reasonable. The following illustration will make this point clearer. Suppose we are measuring a certain length. The errors in our measurements are assumed to be normally distributed with a standard deviation much less than the length we are trying to measure. Hence 20 experiments (or measurements) may be

believed to be sufficient by many persons. In the case of the tossing of a coin, however, the distribution is Bernoullian. Hence not only should we not expect that 20 experiments (or tosses) will suffice in this case too, but we should also not be surprised if the required number comes out to be unsuspectingly bigger than 20. We will now show what can be deduced from the results of tossing a coin a given number of times.

Suppose we toss a coin n times and observe that heads have turned up l times. Two courses are open to us: (1) we can see whether we could have got by random chance alone l heads in n throws assuming that the coin is true; or (2) we can calculate the limits between which lies the chance of getting a head in a random throw of that coin.

Let us take course (1) first. Suppose $l \leq \frac{1}{2}n$. (If $l > \frac{1}{2}n$ the procedure to be adopted is the same but tails are used instead of heads.) Then the chance of getting l or a smaller number of heads in n throws is given by

$$P = I_{\frac{1}{2}}(n-l, l+1) \quad \dots\dots(1),$$

where $I_{\frac{1}{2}}(n-l, l+1)$ is an incomplete β -function ratio written after the manner of Karl Pearson^(a). (i) If neither $n-l$ nor $l+1$ is greater than 50, we can use Pearson's tables^(a) to evaluate P in equation (1). (ii) When either $(n-l)$ or $(l+1)$ or both are greater than 50, we can use a very approximate method which depends upon the fact that the binomial distribution $(\frac{1}{2} + \frac{1}{2})^n$ approaches the corresponding normal distribution very rapidly with the increase in n . It can easily be shown that P is approximately equal to $\{1 - \frac{1}{2}(1 + \alpha)\}$, where $\frac{1}{2}(1 + \alpha)$ corresponds to $x = (n-2l)/\sqrt{n}$ and can be found from table II of reference (3); α and x have the same meaning as in that table.

It has been verified in a large number of cases, to every one of which method (i) could be applied, that the value of P , when not less than 0.001 (i.e. for a range of values which are sufficient for all practical purposes), calculated from (ii) is slightly less than the correct value of P obtained from (i). Almost the whole of this difference appears to be due to the fact that whereas (i) gives the sum of the first $l+1$ terms of the binomial $(\frac{1}{2} + \frac{1}{2})^n$, method (ii) gives, as we might expect, the sum of the first l terms $+ \frac{1}{2}$ of the $(l+1)$ th term of the same binomial. With this correction we get

$$P = 1 - \left\{ \frac{1}{2}(1 + \alpha) \text{ corresponding to } x = (n-2l)/\sqrt{n} \right\} + \frac{n!}{2^{n+1}(n-l)!l!} \quad \dots\dots(2).$$

The necessity for this correction may also be seen from the Euler-Maclaurin formula for replacing a sum by an integral.

Let us select some limit for random chance, say P_1 . Then we consider that our sample of n throws containing l heads could have been obtained by random chance from a true coin if $P < \frac{1}{2}P_1$; the factor $\frac{1}{2}$ is used because we want to treat on the same footing heads and tails obtained from the tossing of a true coin.

We will consider first an example to which both the methods (i) and (ii) are applicable.

Example 1. Out of the first 90 throws of a coin made by Campbell 48* were heads. Could this result have been obtained from a true coin by random chance? Since $48 > \frac{1}{2} \times 90$, we will use the tails instead and see whether we could have obtained by random chance 42 tails in 90 throws of a true coin. Suppose we select 5 per cent as our limit for random chance. Then $P_1 = 0.05$. Let us use method (i) first. From equation (1)

$$P = I_{\frac{1}{2}}(48, 43) = 0.2992,$$

from Pearson's tables^(a).

Let us now use method (ii). We have

$$x = (90 - 2 \times 42) / \sqrt{90} = 0.6324.$$

From tables II of reference (3), $\frac{1}{2}(1 + \alpha)$ corresponding to $x = 0.6324$ is 0.7369. Hence from equation (2) we get

$$P = 1 - 0.7369 + \frac{90!}{2^{91} 48! 42!} \\ = 0.2975.$$

This differs from the true value by 0.0017 only, or by less than 0.6 per cent, showing that method (ii) is quite a good method. Since $P < \frac{1}{2}P_1$ we see that the result of the first 90 throws obtained by Campbell could have been obtained by random chance from a true coin. We will now apply method (ii) to the whole of the 500 throws made by Campbell.

Example 2. 260 heads were obtained in 500 throws. Could this result have been obtained by random chance alone with a true coin? As before we will consider the case of 240 tails in 500 throws. We have to apply method (ii) here. Proceeding as explained in example (1) we get $P = 0.1982$. We thus see that the result could have been obtained with a true coin on the basis of our limit of 5 per cent for random chance.

We have been considering so far that the coin is true. We will now adopt the other course, namely, to find out the nature of the coin from the results of throws. Let us assume as before that in n successive throws of a coin l heads turned up. Suppose the chance of a head turning up in a random trial is k . Then it is shown in reference (4) that

$$k_2 \leq k \leq k_1,$$

where k_2 and k_1 are given by

$$\left. \begin{aligned} P_1 &= I_{k_2}(l, n-l+1) \\ P_1 &= I_{1-k_1}(n-l, l+1) \end{aligned} \right\} \dots\dots(3),$$

the I 's being incomplete β -function ratios. P_1 is the limit for random chance selected by us. When neither $(l+1)$ nor $(n-l+1)$ is greater than 50, it is possible to use a method of evaluating k_1 and k_2 given in reference (4), but for higher values the method of solution is rather tedious and laborious. So we shall apply it to the case where neither $(l+1)$ nor $(n-l+1)$ is greater than 50, that is to the case in example (1) above.

* This number, although determined from figure 1 on p. 802 of Campbells' paper⁽¹⁾ appears to be correct.

Example 3. When a coin was tossed 90 times, the number of heads that turned up was 48. What is the chance of a head turning up in a random trial? Let us choose 5 per cent as our limit for random chance. Then the equations (3) become

$$0.05 = I_{k_2}(48, 43)$$

and

$$0.05 = I_{1-k_1}(42, 49).$$

Solving these in the manner described in reference (4) or otherwise we get $k_2 = 0.39$ and $k_1 = 0.62$. Hence the chance of a head turning up is some fraction between 0.39 and 0.62, these limits being included. From the sample, the chance of a head turning up is $48/90 = 0.533$, and is, naturally, between the limits obtained above.

Coming now to p. 802 of Campbell's paper⁽¹⁾ we see that he distinguishes between two sorts of "collections", to which the application of statistics is admitted to be relevant by him. These, according to him, "are typified respectively by the urn containing black and white balls and the die or the tossed coin". The first sort being finite and enumerable it is possible to know accurately the proportion of members of the different kinds in it. With regard to the second sort he says that it "is not finite or even definite, it is impossible that this proportion should ever be known accurately". His experiment of 500 tosses with a coin was designed to see how many tosses would be required to determine with some accuracy the chance of a head turning up in a random trial. His conclusion stated above is that many more than 500 tosses would be required "to convince anyone that the chance really exists".

Campbell's idea appears to be the following. If the chance of a head turning up when a coin is tossed has a definite value, then this chance calculated from the results of a number of throws of the coin should fluctuate about this definite value as the number of throws is increased, in a manner somewhat similar to, though not so regular as, that of, say, the fluctuations of a dying oscillatory current. Since his figure 2 does not show the least sign of the chance tending to a definite value even when the number of throws is increased to 500, he was led to doubt even the existence of a definite value of the chance. To test Campbell's method of reasoning the following experiment was performed.

Eight marbles of the same size, 4 white and 4 coloured, were put in a cylindrical vessel *A* which was capable of rotation by means of a handle *C*, figure 1. *A* had a circular opening slightly bigger than that required for the marbles to be put in one by one. This opening could be closed by a lid *B*. A draw was made in the following manner. After the opening has been closed *A* is rotated a few times to ensure thorough mixing of the balls. The opening is brought down and the lid pushed aside slowly so that only one marble is allowed to come out. The colour of the marble is noted. This is a draw. For another draw this marble is put back into the vessel, the lid is closed, the vessel is rotated a small number of times and then a marble is drawn out as before. Since there are 4 white and 4 coloured marbles every time before a draw is made, the chance of drawing a white marble is exactly $\frac{1}{2}$. The results of 600 draws are shown in figures 2 and 3.

In these figures the proportion of the number of white marbles drawn in a

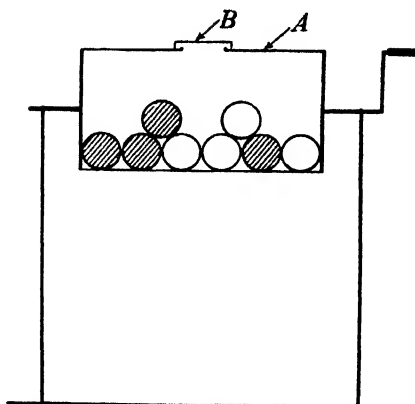


Figure 1.

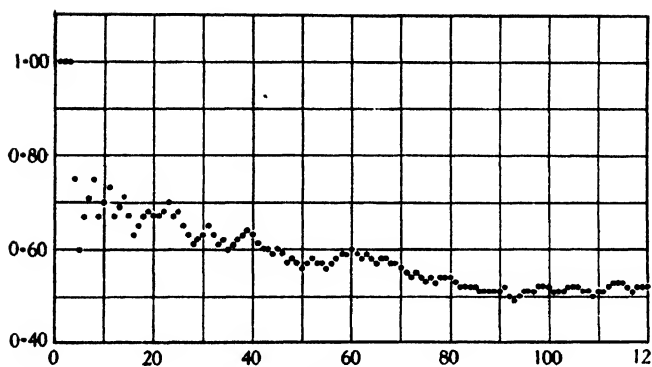


Figure 2.

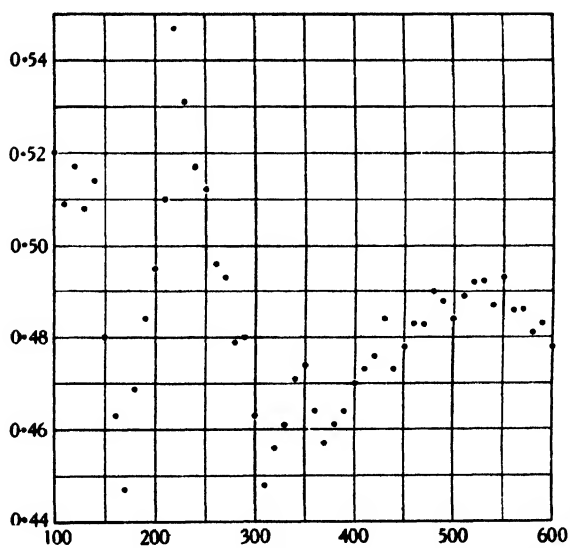


Figure 3.

number of draws is plotted against the number of draws. Campbell's method of reasoning leads us to the deduction that the first 140 draws suggest a chance definitely greater than $\frac{1}{2}$ and the first 600 leave the whole matter doubtful. This is the conclusion reached in the case where we are certain that the chance is definitely $\frac{1}{2}$!

The fallacy in Campbell's method of reasoning lies in the fact that the variations due to random sampling have been overlooked and that their effects, shown in figures 1 and 2 of his paper⁽¹⁾, have been wrongly interpreted as not pointing unequivocally to the existence of a definite chance. In reality his figures 1 and 2 and figures 2 and 3 of this paper should be considered to be quite good illustrations of the fluctuations met with in random sampling.

It is believed, or rather assumed, that in cases similar to those which we have considered above the chance calculated from a sample tends to a limit, which is the true chance, when the sample is increased indefinitely. Two proofs of the accuracy of this assumption have been given by Dorothy Wrinch and Harold Jeffreys⁽⁵⁾ and by M. S. Bartlett⁽⁶⁾. The following proof in which the variations due to random sampling have been taken into account may be found interesting. We have considered the case in which the true, or population, chance is $\frac{1}{2}$. This proof can be adapted to other cases also.

Suppose a sample of n throws of a true coin contains l heads. We will assume, without loss of generality, that $l \leq \frac{1}{2}n$. The chance of obtaining a head is thus l/n as calculated from the sample. This value is subject to random fluctuations. Hence we will restrict ourselves only to those samples, of n random throws each, which could have been obtained with a true coin by random chance. Of this group we will consider only the worst sample, worst in the sense that the chance calculated from it has the greatest difference from the true value. Clearly it is that sample in which l has the smallest value. Let l_1 be this value. Then if P_1 be the limit for random chance selected by us, we have, from equation (2) above,

$$\frac{1}{2}P_1 = 1 - \frac{1}{2}(1 + \alpha)_x + \frac{n!}{2^{n+1}(n-l_1)!l_1!},$$

where $\frac{1}{2}(1 + \alpha)_x$ has been written for " $\frac{1}{2}(1 + \alpha)$ corresponding to $x = (n - 2l_1)/\sqrt{n}$ ". Hence

$$\frac{1}{2}(1 + \alpha)_x = 1 - \frac{1}{2}P_1 + \frac{n!}{2^{n+1}(n-l_1)!l_1!} \quad \dots\dots(4).$$

It has been shown above that the last term on the right-hand side of equation (4) is small in comparison with $\frac{1}{2}P_1$, and since we usually assume that $P_1 = 0.05$ or less, that term will be considerably smaller in comparison with $1 - \frac{1}{2}P_1$. This term being neglected, equation (4) becomes

$$\frac{1}{2}(1 + \alpha)_x = 1 - \frac{1}{2}P_1 \quad \dots\dots(5).$$

Using tables II of reference (3) we can find the corresponding value of x . Let x_1 be this value. But

$$\begin{aligned} x_1 &= \frac{n - 2l_1}{\sqrt{n}}, \\ \therefore \frac{1}{2} - \frac{l_1}{n} &= \frac{x_1}{2\sqrt{n}} \quad \dots\dots(6). \end{aligned}$$

The left-hand side of equation (6) gives the biggest difference that can be expected on the basis of random chance between the true value of the chance and that calculated from our sample. From equation (6) we see that this difference decreases indefinitely as n increases without limit. Hence the chance calculated from a sample tends to the true value in the limit when the sample is increased indefinitely.

Let us denote by d_m the maximum difference obtained on the basis of random chance between the true chance and the chance calculated from a random sample. Equation (6) may now be rewritten as

$$d_m = \frac{x_1}{2\sqrt{n}} \quad \dots\dots(7).$$

If we use 5 per cent as our limit for random chance, x_1 comes out as 1.96. Hence equation (7) becomes

$$d_m = 0.98/\sqrt{n} \quad \dots\dots(8).$$

Suppose we want to know how big the sample should be in order that the chance calculated from it may be correct to within ± 1 per cent. This means that d_m should not exceed 0.005. From equation (8) we see that

$$n \leq \left(\frac{0.98}{0.005}\right)^2, \text{ i.e. } \leq 38,400.$$

Is it surprising then that Campbell's 500 tosses or the 600 draws in the experiment described in this paper were quite inadequate in comparison with the nearly forty thousand experiments that are required?

Let us now apply equation (8) to the experimental result obtained by Campbell, namely that in 500 tosses 260 heads were registered. We have

$$d_m = \frac{0.98}{\sqrt{500}} = 0.044.$$

The actual difference obtained by Campbell is 0.020, which is less than the maximum value that may be expected from random chance. In the case considered in this paper $n=600$, so that

$$d_m = \frac{0.98}{\sqrt{600}} = 0.040.$$

The actual difference observed is 0.022, which is again below the maximum value. Hence we conclude that the samples obtained by Campbell and by us could have been obtained from their respective hypothetical populations by mere chance.

It will be clear from the above that statistical methods, when properly applied, have given us quite definite results in the cases in which Campbell found them to lead to inconclusive results. Campbell's deductions have already been shown to be due to an incorrect interpretation of the experimental values obtained by him and not to any faultiness in the statistical methods themselves. Besides, there do not appear to be any a priori reasons why in other cases also, to which statistical methods are applicable, these methods should not give definite results. Hence Campbell's other point, namely, that it is illegitimate to apply statistical methods to

"problems that arise in drawing conclusions from observations", requires justification. I intend to examine this point in some detail on a future occasion.

In conclusion I wish to thank the referee for having kindly drawn my attention to the two papers (5) and (6).

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DISCUSSION ON PROBABILITY, BASED ON THE PRECEDING PAPER

Mr J. H. AWBERY. In the absence of the author, it falls to me to open this discussion, which as you know is to be a discussion on a field larger than that covered by Savur's paper. I shall take it upon myself to suggest later just how wide it should be.

The paper with which we open arises from one by N. R. Campbell, which in its turn arose from one by Deming and Birge, into the details of which I will not ask you to enter now. But we must consider Campbell's. He was concerned to show that the adjustment of observations is not a subject to which statistics can be applied, because a collection of physical observations is not a sample from some larger collection of measurements-that-were-not-and-never-will-be-made. To illustrate his claim that 20 observations (but note that this word is interpreted in different ways by Campbell and by Savur) are not sufficient to prove the existence of a chance, Campbell gave the results of tossing a coin not 20, but 500 times, and considered that the results do not prove the existence of a chance even here. (Of course, he admits that there *is* a chance, in the neighbourhood of 0.5, but points out that this series does not suffice to prove it.) It is this point, and not his general claim, which is subjected to analysis by Savur, to whose paper we therefore turn.

In the first place, Savur mentions that the number of observations necessary to assess a chance will depend on the nature of the series from which the sample is taken, and in particular on its dispersion. He then proceeds to calculate the chance of obtaining, say, l heads in n throws, and obtains a precise result, which can be evaluated from tables over a certain range of the two variables involved. Outside this range, he contributes a new approximation formula. The author then examines Campbell's results, and finds that they are consistent with a chance of 0.5. Later, he calculates the reverse problem, how many tosses would be necessary to deduce the chance within 1 %, and finds the answer, 38,000. He thus agrees with Campbell that many more than 500 are necessary. Finally, he gives experiments on the drawing of balls from a container, where the chance (the collection being finite) is

not liable to be disputed, and shows that the results, like Campbell's, would fail, on a cursory examination, to suggest any "chance".

His paper also contains another original section, in which a new proof is offered of the proposition that under certain conditions, the chance calculated from a sample tends to a limit, which is the true chance, as the size of the sample is indefinitely increased.

I have tried to give briefly the relation between Campbell's and Savur's papers, and to point out that there are several problems. I suggest that we leave aside the one, "Are statistical methods relevant to the adjustment of observations?", and concentrate on "What information, and with what degree of certainty, can be obtained by examining the results of selecting N objects from a collection which is known to be infinite?"

Dr N. R. CAMPBELL. The author has misunderstood me. I did not assert that ordinary statistical methods were not valid in their own field; or that this field did not include the tossing of a coin. What I said was that they are not applicable to the field that I was discussing, namely the adjustment of divergent measurements of the same magnitude. I said further that one (not the only) reason why they are not so applicable was that the number of observations was not sufficient to determine whether the events were random in the sense in which (in my opinion) events must be random if statistics are to be applicable to them.

How irrelevant Mr Savur's paper is to such a thesis will appear from this example. At 100 tosses I had observed 50 heads and 50 tails. Mr Savur's calculations would make his P a maximum for that distribution. But suppose that the sequence had been regularly heads, tails, heads, tails. . . . That would be, in my opinion, conclusive proof that the events were not random. The evidence on which Mr Savur concludes most definitely that the chance is $\frac{1}{2}$ is the evidence on which I conclude most definitely that there is no chance concerned at all. The reason for the discrepancy is, of course, that Mr Savur assumes what I am concerned to establish, namely that the events are random.

I do not regard the position as materially changed if drawings from an urn are substituted for tosses of a coin. The fact that it is known that there were originally equal numbers of equal balls in the urn does *not* prove that the drawings must be random. For if, during the shaking of the urn, one set of balls wore more rapidly than the other, so that they became smaller, the chance of drawing a ball of this set would progressively increase.

I therefore offer no opinion on the validity of Mr Savur's conclusions; I merely say that they are wholly irrelevant to the particular problem that I was discussing.

Sir ARTHUR EDDINGTON said that the fact that a coin does not come down heads, tails, heads, tails. . . is evidence for the results being random. He considered what can be inferred from a series of coin-tosses. If we tossed 10^{100} times we should learn something about the character of the coin or the manner of tossing, but nothing about probability. Any deviations from the probable result we should interpret as evidence of asymmetry in the coin. We might examine the coin independently

and find it symmetrical, but in that case we might say that the asymmetrical result was due to the volition of the coin itself; if a human being were tossed he would come down feet first oftener than head first. Or more probably we should attribute the result to the experimenter, who must be free to make experimental errors—in this case by failing to toss uniformly. (If Dr Campbell tried to invent ways of making errors instead of the reverse he might produce even stranger results.) There is no general law of errors. If we try to locate a clock pendulum by observing its instantaneous position we obtain a law of error of a kind opposite to the Gaussian law, with fewest observations in the middle of the range. The law of error applicable in each case that arises in practice must be found from theory or experiment. A large number of sources of small error gives the Gaussian law, but systematic errors give other laws. It may be noted that the method of least squares is justifiable for any symmetrical law of error, and not only for the Gaussian law.

Prof. H. DINGLE. My remarks relate to the comparison between coin-tossing and physical experiments. By coin-tossing I mean an operation, not a pure calculation. Both theoretical and practical treatments of probability are important, but they should not be confused. The question, "Does a chance exist?" calls in the former for an existence theorem and in the latter for an action. Mr Savur confuses these demands when, speaking of his experiment, he says on theoretical grounds that a chance of $\frac{1}{2}$ exists, finds by trial no chance of $\frac{1}{2}$, and concludes that the theory is applicable to the experiment. The scientific method is not to assert the existence of something and then look for it, but first to look and then ask if the observations justify the assertion that something exists. That requires a criterion of existence, and I suggest that an experiment reveals the existence of something significant if it gives information about the result of repeating it. Thus, if we weigh a solid, the sum of the numbers on the weights which produce balance is approximately reproduced in a second weighing, and we can therefore deduce the existence of something called "weight", which is measured thereby. With that criterion a coin-toss gives no evidence of a physical existence because, no matter how many times we repeat it, we are still no wiser than before about the result of the next toss. A coin-toss is thus not a physical experiment. But a set of n (say 500) tosses does reveal something significant, because experience shows that the proportion of heads in it enables us to say that the proportion of heads in the next set will lie within a range small compared with the possible range (0 to 1). The observed proportion thus represents (perhaps indirectly) a scientific existence which we may call a "chance". A set of n tosses is thus similar to a physical experiment such as weighing, in that a number of performances gives results showing small deviations from their mean value. Care is necessary, however, in pursuing the comparison, because the source of the deviations is differently located in the two cases. In coin-tossing the instructions (concerning the definition of tossing) are imprecise but can be carried out precisely, whereas in weighing the instructions are precise but can be carried out only imprecisely. Consequently the good experimenter's instinct to make experiments as precise as possible in every respect produces startlingly different results. A strictly specified

tossing machine would give heads (or tails) every time, so that the "chance" would be changed from, say, 0.5 to 1 or 0, whereas if we had a perfect balance, could read the position of the pointer exactly, etc., the "weight" would be only slightly changed.

Dr Campbell's theory of measurement* does not seem general enough to cover all cases, for the range β as defined does not always lie within the range α . Thus, in measuring a small stellar parallax known to be positive, α might range from 0'' to 1'', whereas β would include small negative as well as positive values. This is another example of the failure of a single observation to pass as an experiment, for otherwise the astronomer would be guilty of accepting results known to be impossible and rejecting possible but abnormal ones.

Capt C. W. HUME. I once tossed a man double or quits for a penny stamp, on winning tossed him again, and continued till he owed me £1. 1s. 4d. If Dr Campbell is right in saying that a regular sequence of heads, tails, heads, tails... "would be conclusive proof that the events were not random", I begin to feel uncomfortable.

Colonel J. L. P. MACNAIR. A discussion of this nature is a little dangerous because so many people are discussing different things. The non-scientific user looks to physicists to guide him in his practical problems. I was a little disturbed, for example, by a statement of Prof. Eddington that "you can't determine much from 20 observations of anything". [Prof. Eddington interposed to say that he was referring principally to astronomical observations.] In the science of ballistics and gunnery we build a very useful practical edifice on the results of 5 observations. It is true that those 5 observations are supported by further series obtained under different conditions, but the latter only increase the certainty; they do not invalidate the results reached with a smaller number. In contrast take the example, already mentioned in this discussion, of the determination of the velocity of light. If we look at this over a number of years it seems within the bounds of possibility that we are measuring something which is not really a constant at all. In that case it may well be that the longer we go on observing it, the greater will be the uncertainty.

Mr T. SMITH. It is unnecessary to discuss the author's attitude to Campbell's paper, for it is clearly mistaken. Omitting certain parts of physics where statistical theory is of special significance, I find myself in general agreement with Campbell. Among physicists statistical theory has perhaps been most extensively used to derive a better figure of accuracy than the observations will stand. This is an error of youth; later on, when the experimenter has to be prepared to justify his figures against those of all comers he is usually wise enough to leave such indiscretions behind him. The calculations in this paper illustrate that even very many observations tending closely to a certain result are consistent with facts corresponding to values substantially different. In fact the paper shows how necessary for the physicist some such view as Campbell's is.

* *Proc. Phys. Soc.* 47, 804 (1935).

Two points in the paper call for comment. In the first place there is no essential difference between the two experiments. In saying that the chance of drawing a white marble is exactly $\frac{1}{2}$ the author is counting the marbles just as with the coin he is counting the faces. This fraction must not be confused with the chance the experiments are supposed to reveal, which is the frequency with which certain events occur.

The other point is that we are never concerned with infinity in these questions; any argument in which infinity occurs is of no interest to us. If we considered an infinitely great number of repetitions, we might well argue that in an infinite collection every possible relation between one group and the other would occur at some stage, including those in which the number of heads was negligible compared with the tails and vice versa. I think it was Sir James Jeans who suggested that, given long enough, a group of monkeys provided with typewriters would reproduce all the books in the British Museum.

The author's theoretical discussion appears to be circular in character, but even so he surely claims more than he is entitled to claim. The chance that the ultimate value of his chance (if this has a meaning) will differ substantially from $\frac{1}{2}$ is merely small.

WILFRED W. BARKAS. I understood Dr Campbell to say that if the sequence came heads, tails, heads, tails, for twenty throws he would reject that series in deducing the chance because it would be possible to suppose some ordered outside influence which could contribute to that result. Since this sequence is a possible result of a truly random experiment, it is just as probable as any one other sequence which Dr Campbell would accept as a suitable sequence on which to calculate the 'chance', so it seems to me he is not justified in discarding it and further that an ordered influence might equally well be postulated which would give any sequence which occurred in practice. It seems therefore that it must be the method of calculating the chance which is defective, and this to exactly the degree in which the acceptance of a sequence has to be left to the prejudice of the experimenter. As Mr Smith pointed out, in an infinite series of truly random tosses all possible sequences, including the above, would appear, so a method of calculating the chances should be found which will deal equally well with any of them. The certainty attached to any calculated chance would presumably vary with the number of tosses in the sequence, but not with the order within the sequence.

Mr C. L. T. GRIFFITH. In connexion with the subject of the papers by Mr Norman Campbell and Mr S. R. Savur on coin-tossing it may be mentioned that I made a set of 50,400 draws of a ball from a bowl containing one red, one white and one blue ball, and gave the record to Prof. Egon Pearson at University College, London. The series has been fully abstracted, showing the number of reds in each 10; the number of reds, whites and blues in each 60, 360 etc. sequences; and the progressive deviation from the expected mean for each ball from the start to the end. A diagram is given of these progressive deviations, and has on it the parabola showing the progressive probable errors (not the standard errors). This seems to be a more

expressive diagram than those showing the percentage deviations. Nearly 50 years ago I made many experiments for Karl Pearson which he made use of for his Gresham lectures, and I hope that my more recent and extensive tossing may be used to decide some of the questions considered in the two papers under discussion.

Reply by Mr S. R. SAVUR. I wish to express my warmest thanks to Mr Awbery for having read my paper.

With regard to the general point raised in the discussion, I submit there is fundamentally no difference, from the statistical point of view, between the determination of, say, the length of an object by measurement and that of the chance in the tossing of a coin. In the former case, the various measurements differ among themselves and from the true value, which is assumed to remain constant unless there is a reason to the contrary, on account of unavoidable errors of observation, of unknown magnitude. In the second case the observed values differ from the true chance by unavoidable errors due to random sampling. As it is impossible to find the true value, the aim of the statistical theory in both cases is to use the available results to evaluate, upon certain assumptions, the smallest interval within which the true value lies. The theory asserts that this interval diminishes with the increase in the number of observations and becomes zero when the number is infinite. In my paper I have tried to prove the accuracy of this statement in a special case. This does not, however, mean that statisticians are unpractical enough to demand an infinite number of observations even in a single case; this would be my answer to Mr Smith's remark about infinity. Again, I do not agree with him when he says that the chance, $\frac{1}{2}$, obtained from a count of the marbles in my experiment is different from the chance that the experiments are supposed to reveal.

In his paper⁽¹⁾ Dr Campbell doubted the validity of the application of statistical methods to the adjustment of observations and suggested another method. He also discussed the results of an experiment of 500 tosses of a coin to which, according to him, the application of statistics, although relevant, did not give a definite answer. It appeared to me that I should show first that statistical methods do yield a definite answer, though not the one expected by Dr Campbell, in the case which was considered by him and to which they are applicable. It is only after some such justification that one can try to justify the use of statistical methods in other cases to which their applicability is not immediately obvious. For this reason, therefore, I cannot agree with Dr Campbell's final remark.

Dr Campbell is not right when he says that I conclude "most definitely that the chance is $\frac{1}{2}$ " on the evidence on which he concludes "most definitely that there is no chance concerned at all". All I have concluded is that the results of both experiments are compatible with the assumption of a chance $\frac{1}{2}$ remaining constant throughout; Mr Awbery's remarks are relevant to this point. Similarly, Prof. Dingle's humorous remark that "Mr Savur says on theoretical grounds that a chance of $\frac{1}{2}$ exists, finds by trial no chance of $\frac{1}{2}$, and concludes that the theory is applicable to the experiment" gives a wrong impression about the method used and the conclusions arrived at by me.

It need hardly be mentioned that a "strictly specified tossing machine", visualized by Prof. Dingle, will never be used, even if available, in those cases in which a decision to be made depends upon the result of a toss. For the interest mathematical or otherwise, in the results of tosses as ordinarily carried out is due just to the impossibility of accurately predicting the result of each toss and to the view that in the long run heads and tails will turn up equal numbers of times.

DISCUSSION ON ELECTRON-DIFFRACTION AND SURFACE STRUCTURE

*held at a joint meeting of the Physical Society and the Chemical Society
at Burlington House, 17 March 1938*

Abstract of opening address by Prof. G. I. FINCH, F.R.S. The physical and chemical properties of a solid or liquid depend much on the nature and arrangement of the surface atoms, about which electron-diffraction can give direct information, while as a rule other methods of examination only enable inferences to be drawn. The experimental and interpretative techniques have reached a stage which makes electron-diffraction a powerful means of attack on a wide variety of surface problems, some of which are outlined below.

Mechanical working reduces crystal-size, and, under certain conditions, leads to the formation of amorphous surface films. It is shown that Beilby's view, based on microscopic evidence and according to which the polish layer is amorphous both on metals and on non-metals, is not always correct, since in certain cases the flowed material crystallizes. Evidence afforded by a study of isomorphous overgrowths as to the structure of polish on calcite surfaces is in agreement with that afforded by electron-diffraction. The study of the structure of the polish layer yields information of practical interest to the engineer in connexion with mechanical wear.

Experiments on corrosion show that an amorphous surface film confers as a rule greater protection than a crystalline one. As examples, the oxide films on aluminium, silicon carbide and iron are discussed.

In many instances, electron-diffraction is the sole means of determining the chemical composition of surface films, even the existence of which may be difficult to ascertain by any other method.

The general tendency of electro-deposits is to follow the crystal-size and structure of the basis metal, and this seems to be a determining factor in adhesion. While no clear evidence of alloy formation at the basis metal-deposit interface has so far been observed in electro-deposition, alloys are formed when one metal is chemically displaced by another. Examples are given of cases in which microscopic examination of metallic structures may lead to wrong inferences.

In surface films of the normal paraffins, the long-chain molecules stand vertically on the surface, but in the corresponding end-substituted compounds the molecules lean over to an extent which depends upon the size of the substituent group. The role of such films in lubrication is discussed.

Dr R. BEECHING said that the more widespread employment of electron-diffraction for the attacking of surface problems had been advocated vigorously for some time, and there had, in his opinion, been over-emphasis of the powers and

possibilities of the method, without due regard to the difficulties which may arise. He felt that it must be for the ultimate good of the subject to present these difficulties in their true light.

Quite a number of surfaces give no pattern of any kind. This may be due to a variety of reasons, but it is certainly a severe limitation to the method in some cases. Charging up of the specimen in the electron beam also may constitute such a serious difficulty as sometimes to render the method useless.

In short, invaluable as the method undoubtedly is in some instances, its application is limited in a way which has frequently not been made clear.

A difficulty of another sort—one which has hampered the development of the subject, rather than a difficulty in its application—has been the lack of a satisfactory theory, independent of x-ray diffraction theory. There are a number of points about single crystal patterns which cannot as yet be explained by any existing theory.

Dr A. G. QUARRELL said that since, in general, the surface layers of a specimen cannot be removed with the certainty that no structural or chemical change has been caused by the stripping process, it follows that the reflection method must be used when electron-diffraction is applied to the study of surface structure. Unfortunately, the reflection method is subject to certain limitations from which the transmission method is free. Thus, with polycrystalline reflection specimens a characteristic pattern will result only if crystallites sufficiently thin to transmit electrons project above the general surface. In transmission, the distance from the diffracting crystal to the photographic plate is the same for all crystals, but in the grazing-incidence method there may be a difference in this length equal to the diameter of the specimen. It is for this reason that the diffractions obtained by reflection are never as sharp as those obtained by transmission from a comparable specimen.

Further, in electron-diffraction generally, the diffraction rings of small radius are most useful in determining the structure of the specimen. In the case of α -Fe₂O₃ and Fe₃O₄ the diffractions almost coincide, with the exception of the first two or three rings, and it is essential to use up-to-date technique in order to obtain these rings clear of background.

In view of the importance of determining the spacings of the innermost rings with maximum accuracy, the split-shutter method had been developed for reflection specimens. The reference specimen consists of lead sulphide, freshly precipitated and washed, applied by means of a camel-hair brush to one half of the specimen, and is thus co-planar with the specimen under examination. Lead sulphide has the advantage that it possesses a simple structure and gives a number of rings in the region where accuracy is most desirable.

Since the grazing-incidence method in effect gives the average structure of the strip of specimen traversed by the beam, and since it is not applicable directly to rough surfaces, the possibility of back-reflection of electrons had been examined, the electron beam being normal to the specimen surface. In this way spot patterns had been obtained from a deeply etched iron surface which could not be examined by the reflection method, and a particularly clear spot pattern had been obtained

from a quartz single crystal. It was too early to discuss the mechanism of diffraction involved, but it seemed clear that with further work this should develop into a useful method, applicable where the earlier methods of electron-diffraction fail.

Dr W. COCHRANE. I should like to mention an aspect of the subject which has recently developed—the determination of submicroscopic surface form. The explanation of the irrational interferences observed by various experimenters has always been a perplexing problem, but von Laue's theoretical investigations seem to show that they arise from the nature of the bounding surfaces of the crystals. It is well known that the patterns obtained by electron-diffraction can be interpreted in terms of the hypothetical reciprocal lattice, in which each point represents a plane of the real lattice. A sphere of radius $1/\lambda$ is drawn, where λ is the wave-length of the electrons, and the points of the reciprocal lattice intersected by the sphere appear as spots in the photograph. In general only a few points are intersected. But von Laue has established a rule which says that, if P is a plane bounding surface of the crystal, then a short spike, pointing in a direction normal to P , must be attached to each point of the reciprocal lattice. The sphere then intersects many of these spikes, giving corresponding spots in the pattern. Conversely, we can work back from a given pattern and find the directions of the spikes and thus deduce the bounding surfaces. This, however, will be possible only when the surface of the specimen is fairly uniform and reasonably simple in its topography, for if all sorts of bounding faces are present the effect will be lost.

Some photographs which illustrate this method appeared in the *Proceedings of the Physical Society*, 48 (1936), in the plate facing page 734. Figures 8 and 9 of that plate show the patterns obtained from an electrolytically deposited cobalt surface. The pairs of spots in figure 8 and the groups of fours in figure 9 show that there are here four spikes, although in figure 8 the crystal is set so that the sphere cuts only two of the spikes. It is easily deduced that the surface consists of small projecting lumps bounded by octahedral faces. A view looking down on such a lump is shown in figure 5 of the same paper. Figure 7 of the plate is from an electrolytically deposited nickel surface and here there are only pairs of spots. It is deduced that the surface is composed of rather long corrugations or ridges of triangular cross section. One of these corrugations seen end-on is shown at the bottom of figure 1 of that paper. When these photographs were published, von Laue's theory was not available and I deduced indirectly, from the presence of twin spots, that crystal-growth was taking place very regularly on octahedral faces during the deposition of the metal. This gives a simple physical picture of how the projections are built up. It should be noted, however, that Kirchner has found cases where twinning on octahedral faces occurred but yet the boundaries forming the free surface were cube faces.

By a more detailed and quantitative examination of the patterns von Laue is able also to deduce the size of the projections on the surface, and he finds that their dimensions are about 6×10^{-7} cm. so that their shape could certainly not be distinguished with a microscope.

Dr W. H. J. VERNON, commenting on Prof. Finch's statement that an amorphous surface film confers as a rule greater protection than a crystalline one, remarked that the available evidence (Preston and Bircumshaw's results for aluminium and Prof. Finch's for passivated iron) is scanty so far as metals are concerned; it is, however, supported by recent work on zinc at the Chemical Research Laboratory, done in collaboration with Dr Shearer of the National Physical Laboratory. The physical condition of the initial metal surface is an important factor, but he deprecated the very common misinterpretation of the findings of Bowden and Ridler, to the effect that the melting-point of the metal is necessarily reached, even momentarily, in polishing; actually these workers concluded that the temperature reached is a linear function of load and speed, with the melting-point of the metal as the limiting temperature. He supported Dr Beeching's caution as to the limitations of electron-diffraction methods, notably in respect of the difficulties associated with negative results, and he emphasized the essentially qualitative nature of the information, notwithstanding its great importance and value in specific cases. He urged the closest possible co-operation between electron-diffractionists and those who are applying other methods to the study of these thin films.

Dr J. A. DARBYSHIRE. I would like to describe some results that we have obtained whilst examining oxide-coated cathodes by the electron-diffraction method in the Research Laboratories of Ferranti, Ltd. Oxide cathodes are prepared by spraying a paste, consisting of finely divided mixed crystals of barium and strontium carbonates, or a mechanical mixture of these carbonates, on to a nickel sheath which forms the core of the cathode. This nickel sheath is provided with an internal heating element, and after being sealed into the electron tube the cathode is activated by heat treatment in vacuo. The carbonates decompose into oxides at approximately 800° C., and after they have been flashed for 4 minutes at 1000° C. current is drawn from the cathode at its normal working temperature (about 750° C.) until the thermionic emission reaches a high value.

Various theories have been put forward as to the physical and chemical state of the cathode surface when the emission is a maximum. The theory most generally accepted postulates a monatomic layer of barium resting on the mixed oxides of barium and strontium⁽¹⁾. Electrons are diffracted only by the first 20 atomic layers or so, and it was hoped that they would give some evidence for this surface layer of barium or, in any case, give some interesting information about the outer surface of the cathode⁽²⁾.

The diffraction camera was fitted up so that the cathode could be activated inside the camera and getter pellets could be fired off at suitable stages of the activation. The diffraction photographs from sprayed cathodes in the unactivated state were very poor, and on microscopic examination these surfaces were seen to be quite rough. Much smoother surfaces could be obtained by pouring the mixed carbonate suspension on to the cathode surface and allowing it to dry off in a horizontal position. The photographs of the unactivated carbonates were never very good, but they corresponded to the x-ray patterns and the known structures

for the carbonates, figure 1. The activated cathodes gave much better patterns, figure 2, and well-activated healthy cathodes gave patterns of strontium oxide without any evidence of barium oxide or a solid solution of these oxides. This result corresponds to that obtained by Gaertner. Photographs of cathodes prepared from barium

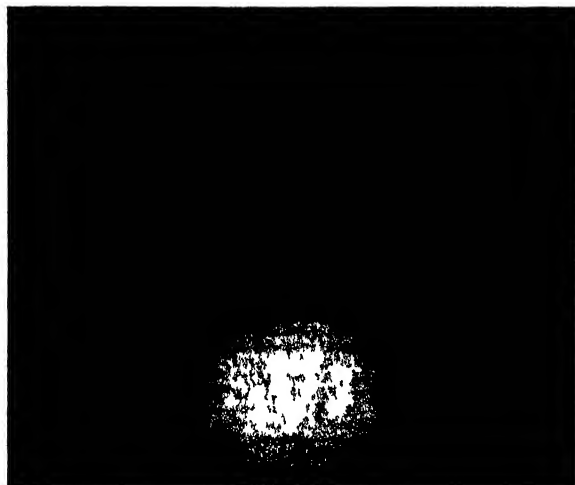


Figure 1.

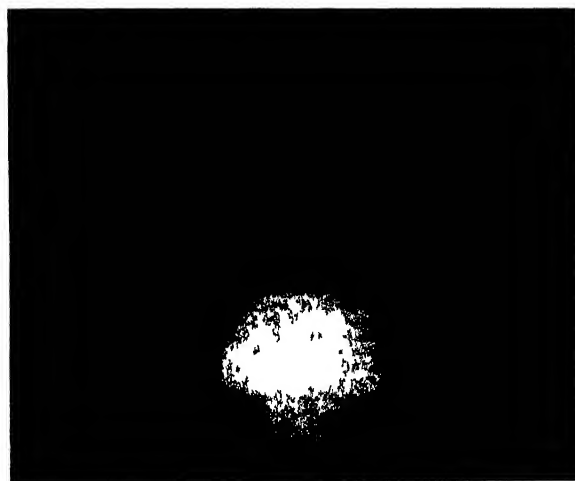


Figure 2

carbonate alone gave barium oxide, and those from strontium carbonate alone gave strontium oxide. The emission from the strontium-carbonate cathodes was very much less than that from the mixed carbonates, although the electron-diffraction patterns indicated strontium oxide in each case. There was no evidence for difference in lattice constant, but the 440 reflection from the strontium oxide of the normal

mixed-carbonate cathode was much stronger than the 440 reflection from ordinary strontium oxide.

The lattice constant of barium is 5.015 Å. and that of strontium oxide is 5.15 Å., and so it is possible that there may be a partial monatomic layer of barium adsorbed to the strontium-oxide lattice, most probably by being bound to the oxygen atoms of the strontium-oxide structure. This may be revealed by a careful comparison of the relative intensity of the lines from the activated strontium-carbonate cathode with those of the normal mixed-carbonate cathode.

Dr H. WILMAN said that in his opinion the experimental technique of electron-diffraction is not very difficult, as Dr Beeching holds it to be. Like all techniques, however, it must be acquired by experience, and all necessary and reasonable care must be taken to avoid adventitious impurities and to study the material under investigation by means of specimens in the form most suited to give clear electron-diffraction patterns.

The use of electron-diffraction to estimate the mean size and shape of crystals can be illustrated by reference to the case of colloidal graphite particles. Reflection patterns yielded by a film adsorbed from the colloidal solution show that the colloidal particles have the normal crystalline structure of graphite. From the large breadths of the diffractions due to planes normal, or nearly normal, to the *c*-axis, the mean crystal thickness in the *c*-axis direction is estimated to be only about 10 carbon-atom layers, whereas planes nearly parallel to the *c*-axis yield sharp diffractions; hence the crystals must measure at least 200 Å. in directions normal to the *c*-axis. Some of the larger of these flake-like crystals can, indeed, be seen in the ultra-microscope, and some even in the ordinary microscope. Patterns obtained by transmission of electrons through the colloidal graphite dried out on a thin collodion film confirm the flake-like form of the crystals in a similar way and show, like the reflection patterns, that the flakes orient themselves parallel to the substrate surface. The appearance of certain abnormal diffraction rings also shows the extreme thinness of a large proportion of the flakes.

It is interesting to note that the x-ray patterns obtained from colloidal graphite are so diffuse as to suggest, entirely erroneously, that the material consists of amorphous carbon. The very diffuse x-ray diffractions yielded by some colloidal clays also are apt to lead to a false view of the particle-form, where the sharp and strong electron-diffraction patterns clearly establish their crystalline flake-like nature.

Dr R. O. JENKINS. Oxide films on molten metals have usually in the past been investigated by removing them from the metal and using transmission electron-diffraction. These films generally show only partial orientation. Examination of the surface of molten metals in vacuo gave reflection patterns consisting of rings and a faint streak, the first from a relatively thick film of oxide and the latter from a very thin film between cracks in the thick film. After the thick film had been swept away by means of a razor blade in vacuo the streak and spot pattern was obtained very strongly. The pattern showed that the metal surface was covered by a very thin

electron-optically flat film of oxide which was always oriented so that the plane on the metal surface was the one with the most metal atoms per unit area. From these patterns it was possible to identify the oxide and calculate its inner potential.

The film on tin just above its melting-point is a tetragonal lattice of SnO resting on its (001) plane, and at a higher temperature is a tetragonal body-centred lattice of SnO₂ resting on its (101) plane. Lead is covered with a film of yellow PbO known as litharge in an orthorhombic lattice resting on its (001) plane, and zinc with a film of ZnO in a hexagonal lattice also resting on its (001) plane. The pattern obtained from bismuth was almost identical in form with that from zinc and indicated a hexagonal-lattice oxide, in which $a=4.0$ Å. and $c/a=1.57$, resting on its (001) plane. This has never been studied with x rays but must almost certainly be Bi₂O₃ isomorphous with the trivalent rare-earth oxides.

When the metal was allowed to cool slowly and form large single crystals it was found that the small oxide crystals had turned under the action of the forces from the underlying metal lattice so that they formed a single-crystal oxide film. This gave a typical single-crystal pattern of spots and Kikuchi lines and showed that the oxide film was still resting on the same plane as before and that movement was only round an axis perpendicular to the metal surface.

THE PRESIDENTS OF THE TWO SOCIETIES, Prof. FERGUSON and Prof. DONNAN, expressed the pleasure and satisfaction which this, the first joint discussion to be held, had given to the members of the two societies.

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OBITUARY NOTICES

DAVID BAXANDALL, A.R.C.S., F.R.A.S.

MR DAVID BAXANDALL, who in April 1934 retired from the position of Deputy Keeper at the Science Museum, passed away on 10 January at the age of 63, after a short illness.

He was born on 9 April 1874, near Keighley in Yorkshire, and received his early education at the Keighley Institute. In 1891 he won a Royal Scholarship with which he proceeded to the Royal College of Science at South Kensington, where his brothers had already preceded him. Here he studied mechanics under Henrici, obtaining his first-class associateship in 1894. He remained at the college as a demonstrator and assisted Lockyer until 1898, when he entered the Science Museum. It was there that he developed a keen interest in early scientific instruments and became a leading authority on the subject, and it is largely due to his unremitting efforts that the collection of scientific instruments and apparatus at the Science Museum is so rich in early and valuable objects.

He was a member of several learned societies, at the meetings of which, however, owing to his natural reticence, he could seldom be persuaded to speak. He contributed a number of papers to the Optical Society, including one on the circular dividing engine of Edward Troughton, and another in which he described two replicas of Galileo telescopes made by Cipriani in Florence.

In May 1923 he presented another paper before the Society on early telescopes. The invention of the station pointer had until recent times been attributed to Nicholson, but Baxandall refuted this claim, and in a concise paper in the *Empire Survey Review* produced evidence that the real inventor was Joseph Huddart, F.R.S.

Mr Baxandall was closely associated for many years with Mr Thomas H. Court, with whom he contributed two articles to the *Proceedings of the Optical Convention* of 1926; one on a "Telescope made by Christopher Cock in 1673", and the other on "Early Optical and other Scientific Instruments as documents of historical value". In the latter paper it was stated that the authors had, during the preceding 20 years, seen and examined many thousands of early microscopes, telescopes and other optical instruments made by English makers. It was an appeal for the preservation of early instruments with reference to some systematic attempts which had been made to acquire, classify and preserve collections.

Mr Baxandall was elected Fellow of the Royal Astronomical Society in 1912, Member of the British Astronomical Association in 1923, and Member of the Optical Society in 1916, while he was also a Member of the Optical Conventions of 1912 and 1926.

He was modest, thorough, and entirely free from pretence, and those with whom he came into contact will remember with admiration the honesty of his nature, and his conscientious devotion to his work.

At the time of his retirement he had been Deputy Keeper in charge of the Science Division of the Science Museum for over 12 years.

H. S.

MR A. M. CODD

MR ARTHUR MORTIMER CODD was born in 1880 and educated at Harrow. He later entered as a student for the electrical engineering course at the Central Technical (now the City and Guilds) College, South Kensington. After completing this course he joined Messrs Johnson and Phillips, Charlton, as a premium pupil, passing through the various shops and drawing offices, and on completion of his training he specialized in inductance and high-frequency apparatus.

In 1906 he began business on his own account as the High Tension Company, renting a small shop at the works of Johnson and Phillips, where he manufactured ignition and inductance coils for medical work. The business was later transferred to Hanway Street, Oxford Street, and finally to Belvedere Road, Westminster, where he was established for many years as a manufacturer of ignition coils, the Echo motor horn, and car-lighting generators. His apparatus for the latter purpose was among the first of its type to be used, and was very successful in the use of permanent magnets for the field and car-lighting dynamos. Mr Codd was one of the pioneers of car lighting by electricity, for his first model, the Mira Magnetolite, was produced as long ago as 1909. The Mira high-tension coils are still in use for naval purposes.

A much needed text-book, *Electrical Ignition for Internal Combustion Engines*, was written by him in 1911, and was the standard work of reference for automobile drivers at that period. The book was followed by *Dynamo Lighting for Motor Cars*, published in 1913. Throughout the War he was engaged in the production of many types of high-tension coils for the services.

Some 14 years ago Mr Codd retired from manufacturing and devoted himself to consulting work. He became an active contributor to the technical journals, the chief subject of his articles being primary batteries and high-tension apparatus.

He was for many years a member of the Physical and Röntgen Societies and a regular exhibitor at the Physical Society's annual exhibitions. His novel and beautiful Wimshurst machine, for supplying current to x-ray tubes and the like, will be remembered by visitors and readers of this journal. The painstaking and valuable work done by pioneers of Mr Codd's type is too easily forgotten, and his death at the height of his activities will be deeply regretted. He leaves a widow and a son and daughter.

C. W. S. CRAWLEY

MR CRAWLEY passed away on 9 November, 1937, aged 79. Although after the War he retired to Charlbury in Oxfordshire, before that he was well known in electrical and motoring circles. Educated at Bonn, he afterwards attended the school of engineering in Hanover Square. He then became an original partner in the firm of Nalder, Crawley and Soames, whose electrical measuring instruments became so well known under the title of N.C.S. in the early days of electric lighting. Mr Crawley was the technical partner in this firm and devoted much time to the construction

of standard instruments, and he improved the methods of calibrating them. Later, Mr Crawley's firm decided to give up the more scientific side of their business in favour of the more commercial, and Mr Crawley left them. From this time, having a modest competence, he rather thought of helping others and advancing the cause of science than of making money for himself, and of this work the following examples will be given.

The Board of Trade Laboratory had, at that time, not long been set up with the view of providing standards for the benefit of the rising electrical industry. While practising as a consulting engineer after his retirement from Nalder Bros. and Co. (now Nalder Bros. and Thompson) he spent much of his time in the Board of Trade Electrical Standards Laboratory, voluntarily assisting Mr Rennie, but practically unknown to anyone in the Board of Trade, except Mr Trotter, Mr Rennie and his assistant. He worked chiefly in the resistance room, making highly accurate comparisons of the standards, some of which had been made by Nalder Bros. and Co. in 1892 for the Electrical Standards Committee of the British Association. The Board of Trade standards had been verified by that committee and deposited under the Order in Council of 1894. From a scientific point of view the work was rather disheartening, for it was known that some of the British Association coils had changed owing to acidity in the paraffin wax used for insulation, and other causes, and the redetermination in absolute value was not within the province of the Board of Trade. Major Cardew and Mr Rennie had used them for comparison with resistances sent to the laboratory for certificates, but the methods and apparatus employed were but little better than the early practice of the British Association Committee.

Mr Crawley presented a master coil to the Board of Trade in 1900, the temperature coefficient of which had been measured with extreme care. He devised the rearrangement of the resistance room, constructed the oil tank, thermoelectric and other temperature apparatus, and thermostats. He recognized that the weak point in most measurements of resistance had been the determination of temperature. At his suggestion Dr Guillaume was asked to procure a thermometer of the highest precision, and M. Tonnelot made one, which was brought from Paris by hand. It was graduated to tenths of a degree, but by optical and thermoelectric methods readings were booked to one thousandth of a degree. Mr Crawley considered that high precision might be attained by measurement of temperature rather than by means of the low temperature coefficients of alloys. He gave scrupulous care to corrections. Among those provided for the thermometer was one for atmospheric pressure, and half seriously he put a scale of thousandths of a degree of temperature on an aneroid barometer. He elaborated the Carey Foster slide-wire bridge until differences of one-fifth of a microhm could be read: a modification of the Nalder pattern was used, allowing the two coils to be compared while they were side by side in the oil bath. He devised build-up boxes for passing from 0 Ω . to 10,000 Ω ., only two mercury cups being used at a time; these and the differential galvanometer and thermostat were designed by him and made while he was with Nalder Bros. and Co.

At the International Conference on Electrical Units and Standards in 1908 Mr Crawley was one of the secretaries, and his fluent knowledge of French and German was a great help to the delegates.

He also knew personally many of the pioneers of the motor-car industry; he helped with trials and in the automobile clubs' survey of the country, which resulted in the first signs for warning and direction being erected.

At this time Mr Crawley lived at Putney, where he had a very complete workshop for electrical and mechanical work, and devoted much time to unobtrusively helping other workers, amongst whom were the late Dr George Forbes, then engaged on designing range-finders.*

Crawley was a strong Unionist, and before the War, when the affairs of Ireland began to reach a critical stage, he joined a Corps of Volunteers who were ready to proceed to Ulster if matters came to a head. They used to drill in the evening in Holland Park, and Crawley was in the habit of going about with a short rifle, in the barrel of which the handle of an old golf club was fixed, in his golf bag.

Shortly after the War had begun, declaring that his age was under 40 (although he was really nearly 60) he succeeded in enlisting in the anti-aircraft force, where his mathematical and mechanical knowledge was useful, and for a long time he was in charge of a battery of anti-aircraft guns on the east coast.

After the War, he and his sister removed to Charlbury in Oxfordshire, where he again set up his laboratory. He had an idea that a great deal could be learnt by study of the minor and more rapid fluctuations of the barometer, and spent a good deal of time in devising a special registering barometer for this purpose.

His recreations were golf and fishing, and he was sufficiently expert to build his own flyfishing rod with its tackle.

With his death passed one of the few remaining men connected with the rise of the modern electrical industry from its early stages.

Mr Crawley became a Life Fellow of the Physical Society in 1895.

G. L. A.

CHARLES-EDOUARD GUILLAUME, 1861-1938

FLEURIER, a small village in the Swiss Jura, ten miles from the French frontier, saw the birth of Charles-Edouard Guillaume. Except for a spell of exile during the French revolution, his family had been living there for three centuries. There his childhood was spent, in the midst of men whose living was derived from agriculture in summer and the making of clocks and watches during the snow season. His father, himself a watchmaker, was his first master. He was fifteen when he first left Fleurier; by 1878 he was a student, and a brilliant one, at the Zürich Polytechnicum. After the completion of this course he became an artillery officer, interesting himself in ballistics. But this did not last.

By 1883 we find him, a lad of 22, entering the Bureau International des Poids et Mesures, an organization which had begun work a few years before. O. J. Broch was then Director. J. René Benoît was one of the most distinguished workers, and

* He also helped the writer in his work on dielectrics for several years.

under his influence the foundations of modern metrology were being built with beautiful honesty and enthusiasm. The following anecdote is not irrelevant, since it gives an indication of the atmosphere which was to surround Guillaume for the rest of his life. In 1889 intercomparisons between the platinum-iridium copies of the International metre were being carried on, and Benoît had been examining the accuracy of a few hundred measurements by the mean-squares method. The concordance was most gratifying, except in a single instance in which an inexplicable discrepancy of $1\ \mu$. was to be found. René Benoît came to luncheon in a state of absolute dejection, and sat munching slowly, repeating, at intervals, with the mechanical precision of a clock: "One *whole* micron! . . . one *whole* micron! . . ."

This delightful man chose Guillaume for his assistant. From 1883 to 1889, studies in thermometry, the determination of the thermal expansions of the standards of length were their chief concerns. In 1889, Guillaume's *Traité Pratique de la Thermométrie de Précision* was published: every metrologist has read this fundamental work. Off and on, Guillaume was to be concerned with thermometric and metrological work all his life, but in 1895, there happened the incident which started him on a series of researches whose initial purpose was purely metrological, but whose consequences became of outstanding importance in metallurgy. The Bureau had long been interested in non-oxidizing alloys, as cheap substitutes for platinum in the making of standards. The Imphy steel works sent Benoît a sample of their NC₄ alloy—a ferronickel containing 24 per cent of nickel; it was found that the thermal expansion of this alloy was actually greater than that of its constituent metals. Some time afterwards, in 1896, Guillaume measured the thermal expansion of an alloy containing 30 per cent of nickel and found it to be half that of pure iron. That day began his patient investigation of the physical properties of ferronickels, which, with the help of the Imphy steel works and his co-workers, chief amongst whom was his pupil Chevenard, progressed for forty years and is indeed still progressing, though its originator is dead. It led successively to the discovery of invar, elinvar and baros; later on, a minute study of the stability conditions of these alloys produced stable invar, universally known and used now; modified elinvar followed as late as 1919 and is now used the world over in the making of spiral watches. Those long studies in physical chemistry are dotted with applications: Guillaume it was who built non-dilatable standards of length, designed the first invar wires for the measurement of geodetic bases, and invented the integral balance for the regularization of watches and chronometers. It is because Guillaume has lived and worked that the Short clock No. 44, with an invar pendulum, of the Paris Observatory had in 1935 a maximum variation of 0.00017 sec. as compared with the mean monthly values.

Since the death of René Benoît in 1915, Guillaume had been director of the Bureau International des Poids et Mesures, and up to his retirement in 1936 much of his time was occupied by the government of this small nation. Under his administration, the Bureau remained flourishing and its traditions were kept. The life of Charles-Edouard Guillaume, both public and private, is inseparable from the Pavillon de Breteuil, its laboratory and its garden: many distinguished men

from many nations visited him there, and found him a simple, courteous, charming and wise man. He was patient and thorough, but not plodding; his metallurgical work often shows brilliant intuition. He was modest, and honours were heaped upon him unsought. A Nobel prize was awarded him in 1920; the Physical Society, before which he delivered the Guthrie lecture, presented him with the Duddell medal in 1928. It is not possible to give here a list of the honours and decorations which he received from everywhere. He loathed advertisement, was a staunch friend and foe, and a man who loved work well done. He used to say that "nothing in Science has so many definitive consequences as the gain of one place in decimals". The incomprehension of the fundamental importance of metrology displayed by some physicists could throw him into fits of rage; on those occasions, he could be caustic. One of our more noisy physicists having one day described metrologists as plodding and short-sighted fellows with few ideas, Guillaume answered that the difference between a metrologist and such a physicist as his interlocutor was the same as between a plough-horse and a racehorse: "When the race is ended, what remains? Dust, a little noise; some money has changed hands. Where the plough-horse has pulled, corn may ripen some day." He was right.

G. A. B.

EMERITUS PROFESSOR WILLIAM STROUD, M.A. (OXON.),
D.SC. (LONDON), HON.D.SC. (LEEDS), F.INST.P.

PROF. STROUD, who was chairman of Messrs Barr and Stroud, Limited, died at Torquay on 27 May 1938 at the age of 78.

As a schoolboy in Bristol he soon gave evidence of outstanding mental ability. He obtained an entrance scholarship to University College, Bristol, in October 1878 at the age of eighteen, and eight months later a Gilchrist Scholarship to Owens College, Manchester. A Brakenbury Science Scholarship took him to Balliol College at the early age of twenty. In the London University examinations and at Oxford his record of first class honours was outstanding. Sir Henry Roscoe described his academic career as a most distinguished one not only in what are called the schools but in the far higher regions of scientific investigation, especially in the subject of electricity.

Professor Jowett, Master of Balliol in 1885, referred to him as a young man of great force of mind and character who might become an original discoverer, and Prof. Kohlrausch, in whose Laboratory at Würzburg he spent one Semester in 1884, refers to his skill and vision in practical work. A portion of the vacation of 1883 was spent in the Physical Laboratory at Heidelberg under the direction of Prof. Quincke.

Soon after his return to England the Yorkshire College in June 1885 lost by resignation Sir Edward Thorpe and Sir Arthur Rücker. Notwithstanding his lack of professorial experience and his youth, for he was only twenty-five, William Stroud was appointed successor to Rücker as Cavendish Professor of Physics. Two months thereafter, in August 1885, he met there for the first time the professor of

engineering, and thus commenced a friendship and association that was only terminated 46 years later by the death of Prof. Archibald Barr.

The first results of their collaboration were a lecture-room projection lantern, and apparatus for the ready production of lantern slides from any book illustrations. Both devices are still extensively used. About the beginning of 1888 they decided to collaborate in research work. In the words of Dr Stroud "the times were very curious—science was in a state of frozen immobility. Almost the only Physics then known was the physics of brass and glass. Mechanically propelled vehicles had a maximum speed of only 3 miles per hour and were compelled by law to be preceded by a man with a red flag. Aviation had been proved impossible by Lord Kelvin. Motor cars were unknown. In a world of pure science X-rays were unknown; radium had not been discovered. Nothing was known about argon and the rare gases in the atmosphere. Electrons, isotopes, quanta and heavy hydrogen had not been heard of, and wireless was in the future. The redeeming feature was that income tax was only 6*d.* in the £ and death duties had not been imposed."

As a first investigation they decided to determine, if possible, with still greater accuracy the mechanical equivalent of heat, but a few months later this intention was abandoned when Prof. Barr saw a War Office advertisement in *Engineering* for an infantry range-finder, preferably single-observer, having an accuracy of 4 per cent at 1000 yards. Although neither knew anything about the subject, they decided to enter for the competition and quickly produced a first rough instrument which at least made them realize how difficult the problem was. In less than a month they applied for a patent for their first range-finder, specification no. 9520/1888. The designs were approved by the War Office but no financial assistance was afforded the inventors. It was a condition of the trials that the instruments should be delivered by 31 December 1888, which left very little time for detailed design and construction.

In view of the difficulty of obtaining satisfactory end prisms, silvered reflectors were employed with disastrous results. The morning of the trials was cloudy. After luncheon, however, the sun emerged and its rays falling on the mirrors distorted them so seriously that the readings were affected. In a few months they were informed by the War Office that the instrument was not suitable for adoption in Her Majesty's Service. The Admiralty, however, regarded the results as promising, and in 1891 invited the inventors to submit an instrument for competitive trial in H.M.S. *Arethusa*.

Watkin's two-observer instrument was rejected as unsuitable owing to the restriction of its effective arc of operation, and the single-observer range-finder of Mallock, the Astronomer Royal, proved less accurate than the Barr and Stroud instrument for which an order for six was soon placed.

When Prof. Barr in 1890 was appointed to the Regius Chair of Engineering at Glasgow it was feared that the collaboration would end, but fortunately, as no restrictions were imposed upon the occupant of the Chair, Prof. Barr was able to carry on the actual work of construction more effectively than he could have done in Leeds. The range-finder was soon adopted by the armies and navies of the

principal world powers, and as the small laboratory and workshop, conveniently established in Ashton Lane between Glasgow University and the house of Dr Barr, could not be satisfactorily extended, the first portion of the present factory was erected at Anniesland. This factory to-day produces not only a great variety of range-finders, submarine periscopes, sights of many kinds, and fire-control gear, but also its own optical glass, of which unusually large discs and blocks are required, and anti-vibration rubber for the naval mountings. Owing to the rapid development of the establishment, satisfactory collaboration by correspondence became difficult, and the presence of Dr Stroud in Glasgow became increasingly necessary. In 1909 he accordingly tendered his resignation of the Cavendish Chair, not only on account of the business, but also in the interests of the university in Leeds, the work of which should, he considered, receive the undivided attention of a younger man prepared to advance with enthusiasm the new physical conceptions of radiant energy. Some time before the death of Dr Barr he found it necessary to seek retirement in the more kindly climate of the south, but later after some persuasion he accepted the vacant chairmanship and found great pleasure in his visits to the scene of so many years' successful scientific and practical activity.

The genial and kindly personality of Prof. Stroud, his ability as a student, his efficiency as a teacher, his unsurpassed capacity for the application of science to industry, and his sympathetic regard for his many employees, are characteristics that have endeared his memory to all who throughout his life were privileged to be associated with him.

J. W. F.

THOMAS SMITHIES TAYLOR

THOMAS SMITHIES TAYLOR laid the foundations of Taylor, Taylor and Hobson, Ltd., 52 years ago, and took an active interest in the business up to the time of his death.

He was first apprenticed to Howard's of Bedford, and later to R. and J. Beck, of London. This apprenticeship involved a ceremony at the Goldsmiths' Hall and conferred the status of Freeman of the City of London upon him. In 1886 he left Messrs Beck and started business for himself in Leicester as a maker of lenses, with a capital of £300. Within a few months he was joined by his brother William, who died last year, and by H. W. Hobson. It was largely owing to his initiative and enthusiasm that when, in 1893, H. D. Taylor, of Cooke and Sons, York, invented the Cooke photographic lens, the manufacture was licensed to Taylor, Taylor and Hobson, Ltd.

He was a member of the Territorial Association, and served during the War in the Royal Army Service Corps, and later he was, for a time, Estate Manager at Bedales School, Hampshire.

In all business matters he was keen and orderly, and in personal contacts he was helpful, kindly and generous to a fault; to all who knew him intimately a fine friend.

A. W.

REVIEWS OF BOOKS

Statistical Physics, by L. LANDAU and E. LIFSHITZ. Translated by D. SCHOENBERG. Pp. viii + 234. (Oxford: Clarendon Press.) 20s. net.

The plan of this book is, roughly speaking, to develop thermodynamics from the statistical point of view introduced by Gibbs. His work is very difficult to understand, partly because he is in the habit of embarking on investigations without stating beforehand where they are to lead, and partly because, when he reaches an important result, he does not point the fact out. Thus a mere restatement of his work would be valuable, but the volume before us contains more than this. It develops its subject in an order dictated by logic and not by our experimental familiarity with various concepts, so that energy and entropy appear before temperature, which presents itself as a mere differential coefficient, proved to be constant throughout a closed system which is in equilibrium.

Systems requiring quantum laws are excluded from the scope of the book, but many problems of which connected accounts cannot easily be found elsewhere are included, such as the theory of the Van der Waals gas, and the thermodynamics of solutions which are not very dilute and of ordered solid solutions.

Attention may be directed to the excellent discussion of the difficulties connected with the principle of increase of entropy and the associated difficulty that in a reversible system we "ought" to be able to reverse the sign of the time, and so obtain changes which obey the mechanical laws and yet, since they retrace the steps by which equilibrium was approached, correspond to a decrease of entropy.

Although it shows a few signs of being a translation from a foreign language, the book is well written, and can be recommended to all students of theoretical physics.

J. H. A.

Physik, by Ing.-Dr P. WESSEL, edited by Dr V. RIEDERER VON PAAR. Pp. xii + 550. (Munich: Ernst Reinhardt.) RM. 4.90.

This German textbook is intended to cover the requirements of students in their first semester at the University, and corresponds approximately to our text books for intermediate students. Its divisions are much the same as those in an English text book of similar standard. The first part deals with mechanics, sound, heat and light, the second with magnetism and electricity and atomic physics, whilst the third is a short résumé of the whole text, together with a collection of formulae and 29 tables. It is interesting to note that in the paragraph on specific heat the calorie is first defined; specific heat then follows as the number of calories required to raise one gramme of a substance 1°C . This we believe to be much preferable to the more usual method adopted in English text books of defining the specific heat as a ratio. Strictly speaking *all* measurements are ratios—ratios of the quantity to some given standard unit; and yet it is usually only the definition of specific heat that is made to include also the definition of the standard unit. (Specific gravity, fortunately, is being gradually dropped in favour of the more rational measurement of density.)

The book should be of help to students seeking a knowledge of technical German. It is written in fairly simple German and is clearly printed, so that with an elementary knowledge of the language and some knowledge of physics a student should be able to follow it quite readily.

H. R. L.

Grimsehl's Lehrbuch der Physik, revised by R. TOMASCHEK. Vol. II, Pt. I. Electromagnetic Field and Optics. 8th ed. Pp. x+866. (Leipzig, B. G. Teubner, 1938.) RM. 26.

No efforts have been spared to keep Grimsehl's text book up to date, both by the inclusion of new matter and by the rewriting of parts of the work where experience has shown that the treatment can be improved. A seven-page article on electron optics is new in this edition, and amplified accounts are given of several other topics. In the revised treatment of electromagnetism, greater stress is laid on Maxwell's equations, but here there is still room for improvement. Somewhere in this book the complete system of Maxwell's equations should be put before the student and he should be shown how these equations lead in a perfectly general way to the differential equation of wave motion.

Taken as a whole, this work can only be described as an excellent text book, excellently produced. Prof. Tomaschek is to be congratulated on maintaining its very high standard.

W. S. S.

Die Physik des 20. Jahrhunderts, by P. JORDAN. 2nd ed. Pp. x+159. (Braunschweig, Vieweg, 1938.) RM. 4.80.

The author sets himself the difficult task of drawing in broad outline a complete picture of modern physics. Details of experiments and mathematical formulations of theory are excluded, and attention is concentrated on the underlying ideas which have given direction to the efforts of physicists from the time of Galileo to the present day. The result is an interesting account of the notions of force and motion, action at a distance and through a medium, ether and relativity, the reality of atoms, the wave-particle dualism, quantum theory, causality and so on. Great stress is laid on the "liquidation of materialism" and the triumph of scientific "positivism", a change of view which obviously has an almost mystical significance for the author. This is particularly apparent in the discussion of the bearing of the recent developments in physics on other aspects of the world picture (*Weltanschauung*) such as religion and the theory of knowledge. The book would be improved by the omission of all such excursions from the domain of physics proper. Another improvement for many readers would be the omission of the remarks on p. 37 which belittle Einstein's achievements in the theory of relativity.

It is something of a feat to have written this book without introducing a single diagram or mathematical symbol, but it is doubtful whether the wider circle of readers whom the author has in mind will find it very easy reading.

W. S. S.

Kontinuierliche Spektren, by W. FINKELNBURG. Pp. xi+368. (Berlin: Julius Springer, 1938.) RM. 33; bound RM. 34.80.

It is fitting that the well-known series of monographs, *Struktur und Eigenschaften der Materie*, which already includes several important works on atomic and molecular spectra such as those by Back and Landé, Hund, Grotrian and Sponer, should now include a comprehensive account of present knowledge of continuous spectra. To physicists, astronomers and chemists this will be especially welcome, since nearly all the available books on either line spectra or band spectra neglect continuous spectra almost entirely. We have already had from the present author very useful monographs on continua in the *Physikalische Zeitschrift*, *Die Physik*, etc., but never have we had in a single volume such a wealth of information on the subject. Every type of continuum is adequately dealt with, and the descriptions are invariably accompanied by the relevant parts of the theory of atomic spectra, both x-ray and optical, and molecular spectra.

After a useful introductory chapter, there are five chapters on atomic electronic continua—the general theory, absorption-limit continua and photo-ionization, electron

recombination and series-limit continua in emission, free-electron continuous radiation and absorption, perturbations. Then follow five chapters on molecular continua—general considerations, theory, typical cases, continua of special diatomic molecules, continua of polyatomic molecules. The next three chapters deal with line-breadths, continua of liquids, solutions and crystals, and temperature and black-body radiations. In the remaining two chapters, dealing entirely with the experimental and technical aspects of the subject, we have a review of observed gas continua (absorption and emission) arranged in chemical groups, and an account of the methods of production of emission continua. The text contains 25 short tables of numerical data and 103 illustrations including intensity-distribution curves, energy-level diagrams, and excellent reproductions of well chosen spectrograms. The book ends with a bibliography containing over 1700 classified references, and adequate indexes of authors and subjects. The page is larger than that used for previous monographs in this series—a decided improvement.

W. J.

Light, by F. BRAY, M.A. 2nd ed. Pp. x + 369. (London: Edward Arnold and Co., 1938.) 7s. 6d.

The first edition of this book, which appeared in 1927, must have become so widely known to teachers and students that it is unnecessary to refer at length here to the scope and purpose of the new edition. In revising the work the author has adopted one of the two sign conventions recommended in the Physical Society's *Report on the Teaching of Geometrical Optics* (1934), in order that focal length may take the same sign as dioptric power. The chosen system is the non-Cartesian one in which real objects and images are regarded as being formed in positive spaces and virtual objects and images in negative spaces; and the author states that this "appeals to boys much more than one based on mathematical usage", i.e. either of the Cartesian systems, the old or the new. It is interesting to note that both the choice and the reason for it are the same as in another recent book of about the same scope, Noakes' *Text-book of Light*, which was reviewed earlier in the present volume of these *Proceedings* (p. 150). Additions have been made to every chapter and the author has had in mind the demand for more up-to-date instruction, mainly in illumination, diffraction and spectra. He has done rightly, in the reviewer's opinion, in placing the rewritten chapter on photometry much later in the book, at the end of Part I (geometrical optics).

It is surprising to find in any optical work, especially one in which a large number of short historical and biographical notes appears, that the author is so completely unaware of the whereabouts of the Rowland ruling engine that the distinguished research professor now using it in its much improved form appears (p. 284) as "Professor Wood of Alberta". In a future edition some of the diagrams, for instance figures 64, 118, 132, 139A, 146 and 228 (a), might be amended, and "travelled slower" (p. 10) be changed to "travelled more slowly". It is to be hoped that none of the copies supplied to the booksellers is as imperfect as the reviewer's copy, in which four pages (pp. v to viii, the preface and part of the table of contents) are duplicated, and two pages (pp. 353-4, giving the first few of the examples from Higher Certificate, Intermediate Science and Scholarship examination questions) are missing.

W. J.

Das Mikroskop, by A. ERINGHAUS. Pp. 156, 83 illustrations. (Berlin and Leipzig: B. G. Teubner.) Price in England RM. 2.70.

This little book is one of a series of mathematical-physical books published by B. G. Teubner of Leipzig and Berlin. Its aim is to give an account of the construction and use of the microscope and of its chief accessories. The underlying theory is clearly and concisely stated in an elementary manner but sufficiently to explain the relation between numerical

aperture and resolving power, and Abbe's experiments on the effects of apertures placed in the upper focal plane of the objective on the resolution of gratings are described. After a very brief examination of the aberrations of the objective and eyepiece, methods of measuring their optical constants and the optical tube-length as well as of testing the definition and resolving power are given.

The description of the actual setting up of the instrument for ordinary observation seems unduly condensed, only some three and a half pages being devoted to it, so that it is doubtful if a beginner would find it sufficient. On the other hand a large number of special uses of the microscope are well, though again perhaps somewhat briefly, described: measurements, monochromatic and dark-ground illumination, the ultramicroscope, the use of ultra-violet light and the fluorescent microscope, as well as such matters as the camera lucida and projection. A further section describes the preparation of objects for observation—staining, section-cutting and mounting. Whilst therefore there is nothing new in this book, it should prove useful for the microscope-user, especially in the more modern and extended applications of the microscope, for which the literature is largely scattered in current periodicals.

R. S. C.

Numerical Problems in Advanced Physical Chemistry, by J. H. WOLFENDEN. Pp. xx + 227. (Oxford: Clarendon Press, 1938.) 7s. 6d. net.

The subjects illustrated by the examples in the book are such as would be dealt with, in part, in advanced lecture courses in physical chemistry. The experiments concerned would be too difficult for the student to carry out, and unless research on them was in progress he would never see them. In such circumstances the value of numerical exercises in conjunction with lecture courses is considerable. Since the book does not give accounts of the underlying theory but gives a table of references to text books on physical chemistry, the author has been able to save much space and deal with more subjects than he otherwise could have done. He has also added useful notes to many of the problems. Many students find it very difficult to get any clear idea of practical applications from the text books and would have welcomed a brief restatement of the underlying principles before attacking the difficult problems in the book. Many of the subjects also are outside the scope of lecture courses which are possible in the limited time available, and some seem to be too highly specialized, as for example the section on crystal structure. The book will appeal most to the student beginning research in physical chemistry and the advanced student with a gift for physical chemistry and able to master the theories from the books referred to. It provides an excellent course in many parts of modern physical chemistry which are not covered in other books, and it will be welcomed by teachers and students. Its excellent printing and binding and low price are also deserving of praise.

J. R. P.

Duodecimal Arithmetic, by GEORGE S. TERRY. Pp. 29£. (London: Longmans, Green and Co., Ltd., 1938.) 3os. net.

This book consists primarily of tables of the commoner numerical functions, square roots, cube roots, reciprocals and so on, of the trigonometrical functions and of logarithms, all based on the duodecimal system in which counting is done by dozens instead of by tens. An introductory section explains the undoubted advantages of such a system, and it is to be regretted that the method is unlikely to come into general use owing to the complexities that would arise from the simultaneous existence of two systems. The author and publishers are to be congratulated on their enterprise in making such an excellently produced book available to those who wish to test the possibilities of duodecimal calculations. It may be noted that the pages of the book are numbered on the duodecimal system.

W. D. W.

Time and its Importance in Modern Thought, by M. F. CLEUGH, with a foreword by L. SUSAN STEBBING. Pp. viii + 308. (London: Methuen and Co.) 12s. 6d. net.

Time, as the writer herself points out, may be considered from many points of view. The physicist finds that events occur in time and finds the puzzle of time linked with that of motion. The psychologist finds that in man's mind is an awareness of the flow of time, and of the passage of events. In particular he finds a general belief that we move in time and meet events, which we then leave behind as in memory; few think of themselves as stationary, with the events passing by. Finally, there is the metaphysics of time. Dr Cleugh takes these aspects in order, with the metaphysics of Kant, Bergson, Alexander, McTaggart and Dunne each examined individually, and then attempts a synthesis of her own, culminating in a chapter on reality and its meaning.

Miss Cleugh is no more helpful than many older philosophers, yet many physicists will find the book interesting. They will find, however, that their interest is held, not as physicists, but because the book shows how philosophy regards some problems which are cognate to, but not identical with, some of their own.

J. H. A.

Under the general heading *Actualités Scientifiques et Industrielles* the Physical Society has received the monographs listed below. Each is written by an authority on his subject and the treatment is, in general, concise and clear. The publishers are Herman and Co., 6 Rue de la Sorbonne, 6, Paris.

- 516. PAUL RENAUD. *Analogies entre les Principes de Carnot, Mayer et Curie*. 10 fr.
- 517. M. HAÏSSINSKY. *Le Polonium*. 12 fr.
- 547. R. RIVAUT. *Contribution a l'Étude des Régions Ionisées de la Haute Atmosphère*. 20 fr.
- 549. LÉON BRILLOUIN. *La Structure des Corps Solides dans la Physique Moderne*. 18 fr.
- 550. LOUIS CARTAN. *Spectrographie de Masse. Les Isotopes et leurs Masses*. 20 fr.
- 621. HÉLÈNE METZGER. *Attraction Universelle et Religion Naturelle chez quelques Commentateurs Anglais de Newton*. 1ère Partie. *Introduction Philosophique*. 12 fr.
- 622. HÉLÈNE METZGER. *Attraction Universelle et Religion Naturelle chez quelques Commentateurs Anglais de Newton*. 2ème Partie. *Newton—Bentley—Whiston—Toland*. 15 fr.
- 623. HÉLÈNE METZGER. *Attraction Universelle et Religion Naturelle chez quelques Commentateurs Anglais de Newton*. 3ème Partie. *Clarke—Cheyne—Derham—Baxter—Priestley*. 25 fr.

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